

# JOURNAL OF THE CHEMICAL SOCIETY.

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## ABSTRACTS OF PAPERS ON ORGANIC, PHYSIOLOGICAL, AND AGRICULTURAL CHEMISTRY.

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## JOURNALS FROM WHICH ABSTRACTS ARE MADE.

The following is a list of Journals from which abstracts are made (directly or indirectly) by the Chemical Society and the Society of Chemical Industry. The abbreviated titles printed in italics represent Journals abstracted by the Chemical Society, those printed in roman type being abstracted by the Society of Chemical Industry. Of the former Journals those indicated by an asterisk are also abstracted by the Society of Chemical Industry.

ABBREVIATED TITLE.	JOURNAL.
<i>Abh. Böhm. Akad.</i> . . . .	Abhandlungen der Böhmisches Akademie.
<i>Abh. Deut. Naturwiss. Med. Ver. Böhmen.</i>	Abhandlungen der Deutschen Naturwissenschaftlichen und Medizinischen Verein, Böhmen.
<i>Acad. Sci. Fennicae</i> . . . .	Acta Societatis Scientiarum Fennicae.
<i>Agric. Bull. F. M. S.</i> . . . .	Agricultural Bulletin of the Federated Malay States.
<i>Agric. J. India</i> . . . . .	Agricultural Journal of India.
<i>Agric. Ledger</i> . . . . .	Agricultural Ledger.
<i>Agric. Res. Inst., Pusa Rep. (Bull.)</i>	Agricultural Research Institute, Pusa, Report and Bulletins.
<i>Allgem. Z. Bierbrau. u. Malzfabr.</i>	Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation.
<i>Amer. J. Bot.</i> . . . . .	American Journal of Botany.
<i>Amer. J. Dis. Children</i> . . . .	American Journal of Diseases of Children.
<i>Amer. J. Pharm.</i> . . . . .	American Journal of Pharmacy.
<i>Amer. J. Physiol.</i> . . . . .	American Journal of Physiology.
<i>Amer. J. Publ. Health</i> . . . .	American Journal of Public Health.
<i>*Amer. J. Sci.</i> . . . . .	American Journal of Science.
<i>Amer. Min.</i> . . . . .	American Mineralogist.
<i>Anal. Fis. Quim.</i> . . . . .	Anales de la Sociedad Española Física y Quimica.
<i>Anal. Soc. Quím. Argentina</i>	Anales de la Sociedad Química Argentina.
<i>*Analyst</i> . . . . .	Analyst.
<i>Annalen</i> . . . . .	Justus Liebig's Annalen der Chemie.
<i>Ann. Bot.</i> . . . . .	Annals of Botany.
<i>Ann. di Bot.</i> . . . . .	Annali di Botanica.
<i>Ann. Chim.</i> . . . . .	Annales de Chimie.
<i>*Ann. Chim. Analyt.</i> . . . .	Annales de Chimie Analytique.
<i>Ann. Falsif.</i> . . . . .	Annales des Falsifications.
<i>Ann. Geol. Min. Russie</i> . . . .	Annuaire de la Géologie et de la Minéralogie de Russie.
<i>Ann. hyg. pub. med. legale.</i>	Annales d'hygiène publique et de médecine légale.
<i>Ann. Inst. Pasteur</i> . . . . .	Annales de l'Institut Pasteur.
<i>Ann. Physik</i> . . . . .	Annalen der Physik.
<i>Ann. Physique</i> . . . . .	Annales de Physique.
<i>Ann. R. Staz. Chim. Agrar. Sperim.</i>	Annali della R. Stazione Chimico Agraria Sperimentale di Roma.
<i>Ann. sci. Univ. Jassy</i> . . . . .	Annales scientifiques de l'Université de Jassy.
<i>Ann. Soc. Geol. Belg.: Publ. rel. au Congo Belge</i>	Annales de la Société géologique de Belgique: Publications relatives au Congo Belge.
<i>Apoth. Zeit.</i> . . . . .	Apotheker-Zeitung.
<i>Arb. Gebiet. Physik, Math. Chem.</i>	Arbeiten aus dem Gebiete der Physik, Mathematik und Chemie.
<i>Arch. Anat. Physiol.</i> . . . .	Archiv für Anatomie und Physiologie.
<i>Arch. Chem. Mikros.</i> . . . .	Archiv Chemie und Mikroskopie.
<i>Arch. Entw.-mech. Org.</i> . . . .	Archiv für Entwicklungsmechanik der Organismen.
<i>Arch. expt. Path. Pharm.</i> . .	Archiv für experimentelle Pathologie und Pharmakologie.
<i>Arch. Farm. sperim. Sci. aff.</i>	Archivio di Farmacologia sperimentale e Scienze affini.
<i>Arch. Fisiol.</i> . . . . .	Archivio di Fisiologia.
<i>Arch. Int. Med.</i> . . . . .	The Archives of Internal Medicine.
<i>Arch. ital. Biol.</i> . . . . .	Archives italiennes de Biologie.
<i>Arch. Med. Pharm. milit.</i> . .	Archives de Médecine et de Pharmacie militaires.
<i>Arch. Néerland.</i> . . . . .	Archives Néerlandaises de sciences exactes et naturelles.

ABBREVIATED TITLE.	JOURNAL.
<i>Arch. Néerland. physiol.</i> .	Archives Néerlandaises de physiologie de l'homme et des animaux.
* <i>Arch. Pharm.</i> . . . .	Archiv der Pharmazie.
<i>Arch. Sci. biol. Petrograd</i> .	Archives des Sciences biologiques, Petrograd.
<i>Arch. Sci. phys. nat.</i> . . .	Archives des Sciences physiques et naturelles.
<i>Arch. Suikerind. Ned. Indie</i>	Archief voor de Suikerindustrie in Nederlandsch-Indië.
<i>Arkiv. Kem. Min. Geol.</i> . .	Arkiv. för Kemi, Mineralogi och Geologi.
* <i>Atti R. Accad. Lincei</i> . . .	Atti della Reale Accademia dei Lincei.
<i>Atti R. Accad. Sci. Torino</i>	Atti della Reale Accademia delle Scienze di Torino.
<i>Atti R. Ist. Veneto Sci.</i> . .	Atti del Istituto Veneto di Scienze, Lettere ed Arti.
<i>Aust. Pharm. Notes</i> . . . .	Australian Pharmaceutical Notes and News.
<i>Beitr. Min. Japan</i> . . . .	Beiträge zur Mineralogie von Japan.
<i>Berg. Hüttenm. Rundsch.</i> . .	Berg- und Hüttenmannisches Rundschau.
* <i>Ber.</i> . . . . .	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Deut. bot. Ges.</i> . . . .	Berichte der Deutschen botanischen Gesellschaft.
* <i>Ber. Deut. pharm. Ges.</i> . .	Berichte der Deutschen pharmazeutischen Gesellschaft.
<i>Ber. Deut. physikal. Ges.</i> . .	Berichte der Deutschen physikalischen Gesellschaft.
<i>Ber. Oberhess. Ges. Natur. Heilkunde.</i>	Berichte der Oberhessischen Gesellschaft für Natur- und Heilkunde zu Giessen.
<i>Ber. Ohara Inst. landw. Forsch.</i>	Berichte des Ohara Instituts für landwirtschaftliche Forschungen.
<i>Ber. Sächs. Ges. Wiss.</i> . . .	Berichte über die Verhandlungen der Sächsischen Gesellschaft der Wissenschaften.
<i>Berlin. Klin. Woch.</i> . . . .	Berliner Klinische Wochenschrift.
* <i>Bied. Zentr.</i> . . . . .	Biedermann's Zentralblatt für Agrikulturchemie und rationalen Landwirtschafts-Betrieb.
<i>Biochem. Bull.</i> . . . . .	Biochemical Bulletin.
* <i>Biochem. J.</i> . . . . .	Biochemical Journal.
* <i>Biochem. Zeitsch.</i> . . . .	Biochemische Zeitschrift.
<i>Bd. of Trade J.</i> . . . . .	Board of Trade Journal.
<i>Bol. Acad. Nac. Ciencias, Cordoba.</i>	Boletín de la Academia Nacional de Ciencias, Cordoba.
* <i>Boll. Chim. farm.</i> . . . .	Bolletino Chimico farmaceutico.
<i>Boll. Soc. Geol. Ital.</i> . . .	Bolletino della Società Geologica Italiana.
<i>Boll. Soc. Med.-Chirurg.</i> . .	Bolletino della Società Medico-Chirurgica, Pavia.
<i>Bot. Centr.</i> . . . . .	Botanisches Centralblatt.
<i>Bot. Gaz.</i> . . . . .	Botanical Gazette.
<i>Brass. Malt.</i> . . . . .	Brasserie et Malterie.
<i>Brau- u. Malzind.</i> . . . .	Brau- u. Malzindustrie.
<i>Braunkohle</i> . . . . .	Braunkohle.
* <i>Brennstoff-Chem.</i> . . . .	Brennstoff-Chemie.
<i>Brewers' J.</i> . . . . .	Brewers' Journal.
<i>Brit. J. Phot.</i> . . . . .	British Journal of Photography.
<i>Brit. Med. J.</i> . . . . .	British Medical Journal.
<i>Brit. Pat.</i> . . . . .	British Patent.
<i>Buletinul Chim.</i> . . . . .	Buletinul Chimie.
<i>Bul. Soc. Chim. România</i> . .	Buletinul Societății de Chimie din România.
<i>Bul. Soc. Romane Stiin.</i> . .	Buletinul Societății Romane de Științe.
<i>Bull. Acad. roy. Belg.</i> . . .	Académie royale de Belgique—Bulletin de la Classe des Sciences.
<i>Bull. Acad. Sci. Cracow</i> . .	Bulletin international de l'Académie des Sciences de Cracovie.
<i>Bull. Acad. Sci. Petrograd.</i>	Bulletin de l'Académie Impériale des Sciences de Petrograd.
<i>Bull. Acad. Sci. Roumaine</i>	Bulletin de la Section Scientifique de l'Académie Roumaine.

ABBREVIATED TITLE.	JOURNAL.
Bull. Agric. Intell. . .	Bulletin of the Bureau of Agricultural Intelligence and of Plant Diseases.
Bull. Assoc. Chim. Sucr. .	Bulletin de l'Association des Chimistes de Sucre et de Distillerie.
Bull. Bureau of Standards (U.S.A.).	Bulletin of the Bureau of Standards (U.S.A.).
<i>Bull. Com. Géol. Finlande.</i>	Bulletin de la Commission Géologique de Finlande.
Bull. Forest Exp. Stat. Meguro.	Bulletin of the Forest Experiment Station, Meguro, Tokyo.
<i>Bull. gén. Thérap.</i> . .	Bulletin général de Thérapeutique médicale, chirurgicale, obstétricale.
<i>Bull. Geol. Inst. Univ. Upsala.</i>	Bulletin of the Geological Institution of the University of Upsala.
<i>Bull. Geol. Soc. Amer.</i> .	Bulletin of the Geological Society of America.
<i>Bull. Geol. Survey, U.S.A.</i>	Bulletin of the U.S. Geological Survey.
<i>Bull. Geol. Survey, West Australia.</i>	Bulletin of the Geological Survey, West Australia.
Bull. Imp. Inst. . .	Imperial Institute Bulletin.
<i>Bull. Johns Hopkins Hospital.</i>	Bulletin of Johns Hopkins Hospital.
Bull. School Mines and Met., Univ. Missouri .	Bulletin of the School of Mines and Metallurgy, University of Missouri.
Bull. Sci. Pharmacol. .	Bulletin des Sciences Pharmacologiques.
* <i>Bull. Soc. chim.</i> . .	Bulletin de la Société chimique de France.
* <i>Bull. Soc. chim. Belg.</i> .	Bulletin de la Société chimique de Belgique.
<i>Bull. Soc. chim. biol.</i> .	Bulletin de la Société de chimie biologique.
Bull. Soc. d'Encour. . .	Bulletin de la Société d'Encouragement pour l'Industrie Nationale.
<i>Bull. Soc. franç. Min.</i> .	Bulletin de la Société française de Minéralogie.
Bull. Soc. Franç. Phot. .	Bulletin de la Société Française de Photographie.
Bull. Soc. Ind. Mulhouse .	Bulletin de la Société Industrielle de Mulhouse.
Bull. Soc. Ind. Nord . .	Bulletin de la Société Industrielle du Nord de la France.
<i>Bull. Soc. Oural. Sci. Nat.</i>	Bulletin de la Société Ouralienne des Amateurs des Sciences Naturelles à Catherineberg.
Bull. Soc. Pharm. Bordeaux	Bulletin des Travaux de la Société de Pharmacie de Bordeaux.
<i>Bull. Wellcome Trop. Res. Lab. Cairo Sci. J.</i> . . .	Bulletin of the Wellcome Tropical Research Laboratory. Cairo Scientific Journal.
Canada Dept. Mines Publ. .	Canada Department of Mines Publications.
* <i>Canadian Chem. J.</i> . .	Canadian Chemical Journal.
<i>Canadian Med. Assoc. J.</i> .	Canadian Medical Association Journal.
Caoutchouc et Gutta-Percha	Le Caoutchouc et le Gutta-Percha.
* <i>Centr. Bakt. Par.</i> . . .	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
<i>Centr. Min.</i> . . .	Centralblatt für Mineralogie, Geologie und Palaeontologie.
Centr. Zuckerind. . .	Centralblatt für Zuckerindustrie.
Ch. of Comm. J. . .	Chamber of Commerce Journal.
<i>Chem. App.</i> . . .	Chemische Apparatur.
<i>Chem. Erde</i> . . .	Chemie der Erde.
Chem. Ind. . . .	Chemische Industrie.
* <i>Chem. and Met. Eng.</i> .	Chemical and Metallurgical Engineering.
* <i>Chem. News</i> . . .	Chemical News.
Chem. Trade J. . .	Chemical Trade Journal.
Chem. Umschau Fett-Ind.	Chemische Umschau über die Fett- und Harz-Industrie.
* <i>Chem. Weekblad</i> . . .	Chemisch Weekblad.
* <i>Chem.-Zeit.</i> . . .	Chemiker-Zeitung.

ABBREVIATED TITLE.	JOURNAL.
<i>Chem. Zeitsch.</i> . . .	Chemische Zeitschrift.
* <i>Chem. Zentr.</i> . . .	Chemisches Zentralblatt.
<i>Chem. and Drug.</i> . . .	Chemist and Druggist.
<i>Chemik Polski</i> . . .	Chemik Polski.
* <i>Chim. et Ind.</i> . . .	Chimie et Industrie.
<i>Collegium</i> . . .	Collegium.
* <i>Compt. rend.</i> . . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
<i>Compt. rend. Soc. Biol.</i> . . .	Comptes rendus hebdomadaires de Séances de la Société de Biologie.
Comptes rend. Trav. Lab. Carlsberg	Comptes rendus des Travaux de Laboratoire de Carlsberg.
D. R. P. . . .	Deutsches Reichs-Patent.
Dept. Chem. S. Australia, Bull.	Department of Chemistry, South Australia, Bulletins.
<i>Deut. med. Woch.</i> . . .	Deutsche medizinische Wochenschrift.
<i>Econ. Geol.</i> . . .	Economic Geology.
<i>Econ. Proc. Roy. Dubl. Soc.</i>	Economic Proceedings of the Royal Dublin Society.
<i>Elektrochem. Zeits.</i> . . .	Elektrochemische Zeitschrift.
<i>Engineering</i> . . .	Engineering.
<i>Eng. and Min. J.</i> . . .	Engineering and Mining Journal.
<i>Exper. Stat. Rec.</i> . . .	Experimental Station Record.
<i>Farber-Zeit.</i> . . .	Färber-Zeitung.
<i>Farben-Zeit.</i> . . .	Farben-Zeitung.
<i>Feuerungstechnik</i> . . .	Feuerungstechnik.
<i>Flora</i> . . .	Flora.
<i>Földtani Közlöny</i> . . .	Földtani Közlöny.
<i>Fr. Pat.</i> . . .	French Patent.
<i>Gas J.</i> . . .	Gas Journal.
<i>Gas World</i> . . .	Gas World.
* <i>Gazzetta</i> . . .	Gazzetta chimica italiana.
<i>Geol. För. Förh.</i> . . .	Geologiska Föreningens i Stockholm Förhandlingar.
<i>Geol. Mag.</i> . . .	Geological Magazine.
<i>Gerber</i> . . .	Gerber.
* <i>Giorn. Chim. Ind. Appl.</i> . .	Giornale di Chimica Industriale, ed Applicata.
<i>Gummi-Zeit.</i> . . .	Gummi-Zeitung.
<i>Handl. Vijft. Nat.</i> . . .	Handelingen van het Vijftende Natuur.
<i>Hawaii Agric. Exp. Stat. Bull.</i>	Hawaii Agricultural Experiment Station Bulletins.
<i>Heart</i> . . .	Heart.
<i>Helv. Chim. Acta</i> . . .	Helvetica Chimica Acta.
<i>Hyg. Rundsch.</i> . . .	Hygienische Rundschau.
<i>Indian J. Med. Res</i> . . .	Indian Journal of Medical Research.
<i>India-rubber J.</i> . . .	India-rubber Journal.
<i>Int. Sugar J.</i> . . .	International Sugar Journal.
<i>Int. Zeitsch. phys.-chem. Biol.</i>	Internationale Zeitschrift für physikalisch-chemische Biologie.
<i>Iron Steel Inst. Carnegie Schol. Mem.</i>	Iron and Steel Institute, Carnegie Scholarship Memoirs.
<i>Jahrb. Geol. Reichsanst.</i> . .	Jahrbuch der geologischen Reichsanstalt.
<i>Jahrb. Min.</i> . . .	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
<i>Jahrb. Min. Beil.-Bd.</i> . . .	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie, Beilage-Band.
<i>Jahrb. Radioaktiv. Elektronik.</i>	Jahrbuch der Radioaktivität und Elektronik.
<i>Jahrb. wiss. Bot.</i> . . .	Jahrbuch für wissenschaftliche Botanik.
<i>Jahresber. Ges. vaterl. Kultur.</i>	Jahresbericht der schlesischen Gesellschaft für vaterländische Kultur.

ABBREVIATED TITLE.	JOURNAL.
<i>Jernk. Ann.</i> . . .	Jern-kontorets Annaler.
* <i>J. Agric. Res.</i> . . .	Journal of Agricultural Research.
* <i>J. Agric. Sci.</i> . . .	Journal of Agricultural Science.
<i>J. Amer. Ceram. Soc.</i> . . .	Journal of the American Ceramic Society.
* <i>J. Amer. Chem. Soc.</i> . . .	Journal of the American Chemical Society.
<i>J. Amer. Leather Chem. Assoc.</i>	Journal of the American Leather Chemists' Association.
<i>J. Amer. Med. Assoc.</i> . . .	Journal of the American Medical Association.
<i>J. Assoc. Off. Agric. Chem.</i>	Journal of the Association of Official Agricultural Chemists.
* <i>J. Biol. Chem.</i> . . .	Journal of Biological Chemistry, New York.
<i>J. Board Agric.</i> . . .	Journal of the Board of Agriculture.
<i>J. Canad. Min. Inst.</i> . . .	Journal of the Canadian Mining Institute.
<i>J. Chem. Ind. Tokyo</i> . . .	See Kōgyō-Kwagaku-Zasshi.
<i>J. Chem. Met. Soc. S. Africa</i>	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
<i>J. Chim. physique</i> . . .	Journal de Chimie physique.
<i>J. Coll. Agric. Tohoku</i> . . .	Journal of the College of Agriculture, Tohoku Imperial University, Japan.
<i>J. Coll. Agric. Tokyo</i> . . .	Journal of the College of Agriculture, Tokyo Imperial University, Japan.
<i>J. Coll. Eng. Univ. Tokyo</i>	Journal of the College of Engineering, University of Tokyo.
* <i>J. Coll. Sci. Tokyo</i> . . .	Journal of the College of Science, Imperial University of Tokyo.
<i>J. Exp. Med.</i> . . .	Journal of Experimental Medicine.
* <i>J. Franklin Inst.</i> . . .	Journal of the Franklin Institute.
<i>J. Gasbeleucht.</i> . . .	Journal für Gasbeleuchtung und Wasserversorgung.
<i>J. gen. Physiol.</i> . . .	Journal of general Physiology.
<i>J. Genetics</i> . . .	Journal of Genetics.
<i>J. Geol.</i> . . .	Journal of Geology.
<i>J. Geol. Soc. Tokyo</i> . . .	Chishitsugaku Zasshi (Journal of the Geological Society of Tokyo).
<i>J. Hygiene</i> . . .	Journal of Hygiene.
* <i>J. Ind. Eng. Chem.</i> . . .	Journal of Industrial and Engineering Chemistry.
* <i>J. Ind. Inst. Sci.</i> . . .	Journal of the Indian Institute of Science.
<i>J. Inst. Brewing</i> . . .	Journal of the Institute of Brewing.
<i>J. Inst. Petroleum Tech.</i> . . .	Journal of the Institute of Petroleum Technologists.
<i>J. Landw.</i> . . .	Journal für Landwirtschaft.
<i>J. Marine Biol. Assoc. U.K.</i>	Journal of the Marine Biological Association of the United Kingdom.
<i>J. Med. Res.</i> . . .	Journal of Medical Research.
<i>J. Path. Bact.</i> . . .	Journal of Pathology and Bacteriology.
<i>J. Opt. Soc. Amer.</i> . . .	Journal of the Optical Society of America.
* <i>J. Pharm. Chim.</i> . . .	Journal de Pharmacie et de Chimie.
<i>J. Pharm. Expt. Ther.</i> . . .	Journal of Pharmacology and Experimental Therapeutics.
* <i>J. Physical Chem.</i> . . .	Journal of Physical Chemistry.
<i>J. Physiol.</i> . . .	Journal of Physiology.
<i>J. Physiol. Path. gén.</i> . . .	Journal de Physiologie et de Pathologie générale.
* <i>J. pr. Chem.</i> . . .	Journal für praktische Chemie.
<i>J. Proc. Asiatic Soc. Bengal.</i>	Journal and Proceedings of the Asiatic Society of Bengal.
<i>J. Roy. Agric. Soc.</i> . . .	Journal of the Royal Agricultural Society.
<i>J. Roy. Army Med. Corps</i> . . .	Journal of the Royal Army Medical Corps.
<i>J. Roy. Hort. Soc.</i> . . .	Journal of the Royal Horticultural Society.
<i>J. Roy. Soc. New South Wales.</i>	Journal and Proceedings of the Royal Society of New South Wales.
<i>J. Roy. Soc. West Australia</i>	Journal of the Royal Society of West Australia.

ABBREVIATED TITLE.	JOURNAL.
* <i>J. Russ. Phys. Chem. Soc.</i>	Journal of the Physical and Chemical Society of Russia.
<i>J. Scot. Met. Soc.</i>	Journal of the Scottish Meteorological Society.
<i>J. Soc. Arts</i>	Journal of the Royal Society of Arts.
<i>J. Soc. Dyers and Col.</i>	Journal of the Society of Dyers and Colourists.
<i>J. Soc. Leather Trades Chem.</i>	Journal of the Society of Leather Trades Chemists.
<i>J. Soc. Glass Technology</i>	Journal of the Society of Glass Technology.
<i>J. S. African Assoc. Anal. Chem.</i>	Journal of the South African Association of Analytical Chemists.
<i>J. Textile Inst.</i>	Journal of the Textile Institute.
<i>J. Usines Gaz</i>	Journal des Usines à Gaz.
<i>J. Washington Acad. Sci.</i>	Journal of the Washington Academy of Science.
<i>J. West Scotland Iron Steel Inst.</i>	Journal of the West of Scotland Iron and Steel Institute.
<i>K. Svenska Vet.-Akad. Handl.</i>	Kongliga Svenska Vetenskaps Akademiens Handlingar.
<i>Kentucky Exp. Stat. Bull.</i>	Kentucky Experimental Station, Bulletin.
<i>Keram. Rundsch.</i>	Keramisch Rundschau.
<i>Kew Bull.</i>	Kew Bulletin.
<i>Kongl. Landtbr. Handl. Tidskr.</i>	See Bull. Agric. Intell.
<i>Kōgyō-Kwagaku-Zasshi (J. Chem. Ind. Japan).</i>	Kōgyō-Kwagaku-Zasshi (Journal of Chemical Industry, Japan).
* <i>Kolloid Zeitsch.</i>	Kolloid Zeitschrift.
* <i>Koll. Chem. Beihefte</i>	Kolloid-chemische Beihefte.
<i>Kosmos</i>	Kosmos (Lemberg).
<i>Kühn-Archiv</i>	Kühn-Archiv.
<i>Kunststoffe</i>	Kunststoffe.
<i>Lancet</i>	The Lancet.
<i>Landw. Jahrb.</i>	Landwirtschaftliche Jahrbücher.
<i>Landw. Versuchs.-Stat.</i>	Die landwirtschaftlichen Versuchs-Stationen.
<i>Leather Trades Rev.</i>	Leather Trades Review.
<i>Le Radium</i>	Le Radium.
<i>Local Govt. Bd. Reports</i>	Local Government Board Reports.
<i>Louisiana Bull.</i>	Louisiana Bulletin.
<i>Louisiana Planter</i>	Louisiana Planter.
<i>Lunds Univ. Arsskr.</i>	Lunds Universitets Års-skrift.
<i>Math. és Termész. Ért.</i>	Mathematikai és Természettudományi Értesítő, Budapest.
<i>Medd. K. Vetenskapsakad. Nobel-Inst.</i>	Meddelanden från Kongl.-Vetenskapsakademiens Nobel-Institut.
<i>Medd. on Grönland</i>	Meddelser on Grönland.
<i>Med. Chron.</i>	Medical Chronicle.
<i>Med. Klinik</i>	Medizinesche Klinik.
<i>Mem. Acad. Sci. Petrograd.</i>	Mémoires de l'Académie Impériale des Sciences de Petrograd.
<i>Mem. Accad. Lincei</i>	Memorie della Reale Accademia dei Lincei.
<i>Mem. Accad. Sci. Torino</i>	Memorie della Reale Accademia delle Scienze di Torino.
<i>Mem. Coll. Sci. Kyōtō</i>	Memoirs of the College of Science, Kyōtō Imperial University.
<i>Mem. Coll. Sci. and Eng. Kyōtō Imp. Univ.</i>	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
<i>Mem. Dept. Agric. India</i>	Memoirs of the Department of Agriculture in India.
<i>Mem. Manchester Phil. Soc.</i>	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
<i>Mem. Soc. Ing. Civ.</i>	Mémoires de la Société des Ingénieurs Civils de France.
<i>Mem. Soc. Natur. Kiev</i>	Mémoires de la Société des Naturalistes de Kiev.



ABBREVIATED TITLE.	JOURNAL.
<i>Mem. Soc. Toscana Sci. Nat.</i>	Memorie della Società Toscana di Scienze naturali residente in Pisa.
<i>Metall u. Erz</i> . . . .	Metall und Erz.
<i>Metrop. Water Bd. Rep.</i> . . . .	Metropolitan Water Board Reports.
<i>Milch. Zentr.</i> . . . .	Milchwirtschaftliches Zentralblatt.
<i>Min. Mag.</i> . . . .	Mineralogical Magazine and Journal of the Mineralogical Society.
<i>Mitt. geol. Landesanst.</i> . . . .	Mittheilungen der geologischen Landesanstalt von Elsass-Lothringen.
<i>Mitt. Inst. Kohlenw.</i> . . . .	Mittheilungen des Institutes für Kohlenvergasung und Nebenproduktergewinnung.
<i>Mitt. k. Materialprüf.</i> . . . .	Mittheilungen aus dem königlichen Materialprüfungsamt zu Gross-Lichterfelde West.
<i>Mitt. med. Ges. Tokyo</i> . . . .	Mittheilungen der medizinischen Gesellschaft zu Tokyo.
<i>Mitt. Naturforsch. Ges. Halle.</i>	Mittheilungen der Naturforschenden Gesellschaft zu Halle.
<i>*Monatsh.</i> . . . .	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
<i>Monatsh. Math. Physik</i> . . . .	Monatshefte für Mathematik und Physik.
<i>*Mon. Sci.</i> . . . .	Moniteur Scientifique.
<i>Month. Not. Roy. Astr. Soc.</i>	Monthly Notices of the Royal Astronomical Society, London.
<i>Münch. med. Woch.</i> . . . .	Münchener medizinische Wochenschrift.
<i>Nachr. Ges. Wiss. Göttingen.</i>	Nachrichten von der königlichen Gesellschaft der Wissenschaften zu Göttingen.
<i>Nature</i> . . . .	Nature.
<i>Naturwiss.</i> . . . .	Die Naturwissenschaften.
<i>Naturw. Rdsch.</i> . . . .	Naturwissenschaftliche Rundschau.
<i>New York Agr. Expt. Sta. Bull.</i>	New York Agricultural Experiment Station Bulletins.
<i>New Zealand Dominion Laby. Rept.</i>	New Zealand Dominion Laboratory Reports.
<i>New Zealand Jnl. of Science and Technology</i>	New Zealand Journal of Science and Technology.
<i>Nova Acta Soc. Sci.</i> . . . .	Nova Acta Regiæ Societatis Scientiarum Upsaliensis.
<i>Nuovo Cim.</i> . . . .	Il Nuovo Cimento.
<i>Öfvers. Finska Vet.-Soc.</i> . . . .	Öfversigt af Finska Vetenskaps-Societetens Förhandlingar, Helsingfors.
<i>*Oesterr. Chem.-Zeit.</i> . . . .	Oesterreichische Chemiker-Zeitung.
<i>Oil and Colour Trades J.</i> . . . .	Oil and Colour Trades Journal.
<i>Oil, Paint, and Drug Rep.</i> . . . .	Oil, Paint, and Drug Reporter.
<i>Oversigt Danske Vid. Selsk.</i>	Oversigt over det Kongelige Danske Videnskabernes Selskab Forhandlingar.
<i>Pahasapa Quart.</i> . . . .	Pahasapa Quarterly.
<i>Paper</i> . . . .	Paper.
<i>Papierfabr.</i> . . . .	Papier-Fabrikant.
<i>Perf. and Essent. Oil Rec.</i> . . . .	Perfumery and Essential Oil Record.
<i>Per. spis. Sofia</i> . . . .	Periodicesko spisanie Sofia.
<i>Petroleum</i> . . . .	Petroleum.
<i>Pflüger's Archiv.</i> . . . .	Archiv für die gesammte Physiologie des Menschen und der Thiere.
<i>Pharm. J.</i> . . . .	Pharmaceutical Journal.
<i>*Pharm. Weekblad</i> . . . .	Pharmaceutisch Weekblad.
<i>*Pharm. Zentr.-h.</i> . . . .	Pharmazeutische Zentralhalle.
<i>Phil. Mag.</i> . . . .	Philosophical Magazine (The London, Edinburgh and Dublin).
<i>Phil. Trans.</i> . . . .	Philosophical Transactions of the Royal Society of London.

ABBREVIATED TITLE.	JOURNAL.
Philippine J. Sci. . . . .	Philippine Journal of Science.
Phot. J. . . . .	Photographic Journal.
Phot. Korr. . . . .	Photographische Korrespondenz.
Physical Rev. . . . .	Physical Review.
Physikal. Zeitsch. . . . .	Physikalische Zeitschrift.
Proc. Amer. Phil. Soc. . . . .	Proceedings of the American Philosophical Society.
Proc. Amer. Physiol. Soc. . . . .	Proceedings of the American Physiological Society.
*Proc. Amer. Soc. Biol. Chem. . . . .	Proceedings of the American Society of Biological Chemists.
Proc. Amer. Soc. Civ. Eng. . . . .	Proceedings of the American Society of Civil Engineers.
Proc. Amer. Soc. Testing Materials . . . . .	Proceedings of American Society for Testing Materials.
Proc. Austral. Inst. Min. Eng. . . . .	Proceedings of the Australasian Institute of Mining Engineers.
Proc. Camb. Phil. Soc. . . . .	Proceedings of the Cambridge Philosophical Society.
Proc. Durham Phil. Soc. . . . .	Proceedings of the Durham Philosophical Society.
Proc. Eng. Soc. W. Pa. . . . .	Proceedings of the Engineers' Society of Western Pennsylvania.
Proc. Inst. Civ. Eng. . . . .	Proceedings of the Institution of Civil Engineers.
Proc. Inst. Mech. Eng. . . . .	Proceedings of the Institution of Mechanical Engineers.
Proc. Inst. Min. and Met. . . . .	Proceedings of the Institution of Mining and Metallurgy.
*Proc. K. Akad. Wetensch. Amsterdam. . . . .	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Nat. Acad. Sci. . . . .	Proceedings of the National Academy of Sciences.
Proc. Nova Scotia Inst. Sci. . . . .	Proceedings of the Nova Scotia Institute of Science.
Proc. Phil. Soc. Glasgow . . . . .	Proceedings of the Glasgow Philosophical Society.
Proc. Physical Soc. . . . .	Proceedings of the Physical Society of London.
Proc. Physiol. Soc. . . . .	Proceedings of the Physiological Society.
Proc. Roy. Inst. . . . .	Proceedings of the Royal Institution of Great Britain.
Proc. Roy. Irish Acad. . . . .	Proceedings of the Royal Irish Academy.
*Proc. Roy. Soc. . . . .	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin. . . . .	Proceedings of the Royal Society of Edinburgh.
Proc. Roy. Soc. Med. . . . .	Proceedings of the Royal Society of Medicine.
Proc. Roy. Soc. Queensland . . . . .	Proceedings of the Royal Society of Queensland.
Proc. Roy. Soc. Tasmania . . . . .	Proceedings of the Royal Society of Tasmania.
Proc. Soc. Exp. Biol. Med. . . . .	Proceedings of the Society for Experimental Biology and Medicine.
Proc. U.S. Nat. Mus. . . . .	Proceedings of the United States National Museum.
Proc. verb. Soc. Toscana Sci. Nat. . . . .	Processi verbali Società Toscana di Scienze Naturali.
Pulp and Paper Magazine . . . . .	Pulp and Paper Magazine.
Quart. J. Exp. Physiol. . . . .	Quarterly Journal of Experimental Physiology.
Quart. J. Geol. Soc. . . . .	Quarterly Journal of the Geological Society.
Quart. J. Med. . . . .	Quarterly Journal of Medicine.
Radium in Biol. Heilkunde . . . . .	Radium in Biologie und Heilkunde.
Rec. Australian Mus. . . . .	Records of the Australian Museum.
Rec. trav. bot. Néerland. . . . .	Recueil des travaux botaniques Néerlandaises.
*Rec. trav. chim. . . . .	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rend. Accad. Sci. Fis. Mat. Napoli. . . . .	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche, Napoli.
Rend. Ist. Lomb. Sci. Lett. . . . .	Rendiconti dell' Istituto Lombardo di Scienze e Lettere.
Rend. Soc. Chim. Ital. . . . .	Rendiconto della Società Chimica Italiana.
Rep. Aust. Assoc. Sci. . . . .	Report of the Australian Association for the Advancement of Science.

ABBREVIATED TITLE.	JOURNAL.
<i>Rep. Brit. Assoc.</i>	Report of the British Association for the Advancement of Science.
<i>Rev. gén. Bot.</i>	Revue générale de Botanique.
<i>Rev. Gén. Mat. Col.</i>	Revue Générale des Matières Colorantes.
<i>Rev. Mét.</i>	Revue de Métallurgie.
<i>Rev. Real Acad. Ciencias exact. Madrid.</i>	Revista de la Real Academia de Ciencias exactas, Físicas y Naturales de Madrid.
<i>Riv. Min. Crist. Ital.</i>	Rivista di Mineralogia e Cristallografia Italiana.
<i>Sbornik Klubu Pri.</i>	Sbornik Klubu Prirodovedeckeho (Prague).
<i>Schweiz. Apoth. Zeit.</i>	Schweizerische Apotheker Zeitung.
<i>Schweiz. Chem. Zeit.</i>	Schweizerische Chemiker Zeitung.
<i>Science.</i>	Science.
<i>Scient. Amer.</i>	Scientific American.
<i>*Sci. Ind. Rep. Roure-Bertrand Fils.</i>	Scientific and Industrial Reports of Roure-Bertrand Fils.
<i>Sci. Proc. Roy. Dubl. Soc.</i>	Scientific Proceedings of the Royal Dublin Society.
<i>Sci. Rep. Tohoku Imp. Univ.</i>	Science Reports, Tohoku Imperial University.
<i>Sci. Trans. Roy. Dubl. Soc.</i>	Scientific Transactions of the Royal Dublin Society.
<i>Seifenfabr.</i>	Der Seifenfabrikant.
<i>Seifensied. Zeit.</i>	Seifensieder Zeitung.
<i>Sitzungsber. Akad. München.</i>	Sitzungsberichte der bayerischen Akademie der Wissenschaften zu München.
<i>Sitzungsber. Akad. Wiss. Wien.</i>	Sitzungsberichte der Akademie der Wissenschaften, Wien.
<i>Sitzungsber. Ges. Naturwiss. Marburg.</i>	Sitzungsberichte der Gesellschaft zur Beförderung der gesammten Naturwissenschaften in Marburg.
<i>Sitzungsber. Heidelberger Akad. Wis.</i>	Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
<i>Sitzungsber. Med. Naturwiss. Ges. Münster.</i>	Sitzungsberichte der Medizinisch-Naturwissenschaftlichen Gesellschaft zu Münster-in-Westfalens.
<i>Sitzungsber. Naturforsch. Ges. Petrograd.</i>	Sitzungsberichte der Naturforschenden Gesellschaft zu Petrograd.
<i>Sitzungsber. Naturforsch. Ges. Rostock.</i>	Sitzungsberichte der Naturforschenden Gesellschaft zu Rostock.
<i>Sitzungsber. phys. med. Ges. Erlangen.</i>	Sitzungsberichte der physikalisch-medizinischen Gesellschaft zu Erlangen.
<i>Sitzungsber. Preuss. Akad. Wiss. Berlin.</i>	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
<i>Skand. Arch. Physiol.</i>	Skandinavisches Archiv für Physiologie.
<i>Smithsonian Miscell. Coll.</i>	Smithsonian Miscellaneous Collections.
<i>*Soil Sci.</i>	Soil Science.
<i>South African J. Sci.</i>	South African Journal of Science.
<i>Sprechsaal.</i>	Sprechsaal.
<i>Stahl u. Eisen.</i>	Stahl und Eisen.
<i>Staz. sper. agr. ital.</i>	Stazioni sperimentali agrarie italiane.
<i>Strahlenther.</i>	Strahlentherapie.
<i>Suom. Tied. Toim.</i>	Suomalaisen Tiedeakatemia Toimituksia.
<i>Svensk Kem. Tidskr.</i>	Svensk Kemisk Tidskrift.
<i>T.</i>	Transactions of the Chemical Society.
<i>Tekn. Tidsk.</i>	Teknisk Tidskrift.
<i>Ther. Gegenw.</i>	Die Therapie der Gegenwart.
<i>Ther. Monatsh.</i>	Therapeutische Monatshefte.
<i>Times Eng. Suppl.</i>	Times Engineering Supplement.
<i>Tonind.-Zeit.</i>	Tonindustrie-Zeitung.
<i>Trans. Amer. Electrochem. Soc.</i>	Transactions of the American Electrochemical Society.
<i>Trans. Amer. Inst. Chem. Eng.</i>	Transactions of the American Institute of Chemical Engineers.
<i>Trans. Amer. Inst. Metals.</i>	Transactions of the American Institution of Metals.

ABBREVIATED TITLE.	JOURNAL.
Trans. Amer. Inst. Min. Eng.	Transactions of the American Institute of Mining Engineers.
Trans. Ceram. Soc. . . .	Transactions of the English Ceramic Society.
*Trans. Faraday Soc. . . .	Transactions of the Faraday Society.
Trans. Inst. Metals . . .	Transactions of the Institute of Metals.
Trans. Iron and Steel Inst.	Transactions of the Iron and Steel Institute.
Tr. N. Eng. Inst. Min. and Met.	Transactions of the North of England Institute of Mining and Metallurgy.
Trans. New Zealand Inst. . .	Transactions of the New Zealand Institute.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Path. Soc. . . .	Transactions of the Pathological Society.
Trans. Roy. Irish Acad. . .	Transactions of the Royal Irish Academy.
Trans. Roy. Soc. Canada . .	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. Edin. . .	Transactions of the Royal Society of Edinburgh.
Trav. Mus. Geol. Acad. Sci. Petrograd.	Travaux de Musée Géologique près l'Académie Impériale des Sciences de Petrograd.
Trav. Soc. Natur. Petrograd .	Travaux de la Société Impériale des Naturalistes de Petrograd.
Tsch. Min. Mitt. . . .	Tschermak's Mineralogische Mitteilungen.
U.S. Bureau of Mines, Bull. and Tech. Papers.	United States Bureau of Mines, Bulletins and Technical Papers.
U.S. Bureau Plant Ind. . .	United States Bureau of Plant Industry.
U.S. Comm. Rept. . . .	United States Commerce Reports, Daily Consular and Trade Reports.
U.S. Dept. Agric. Bull. . .	United States Department of Agriculture Bulletins.
U.S. Hyg. Labor. Bull. . .	United States Hygienic Laboratory Bulletins.
U.S. Pat. . . . .	United States Patent.
Univ. Illinois Bull. . . .	University of Illinois Bulletins.
Utah Agric. Coll. Exper. Stat. Bull.	Utah Agricultural College Experiment Station Bulletins.
Verh. Geol. Reichsanst. Wien.	Verhandlungen der geologischen Reichsanstalt in Wien.
Verh. Ges. deut. Naturforsch. Aertze.	Verhandlungen der Gesellschaft deutscher Naturforscher und Aertze.
Verh. Naturhist. med. Ver. Heidelberg.	Verhandlungen des naturhistorisch-medizinischen Vereins zu Heidelberg.
Verh. Naturhist. Rheinl. . .	Verhandlungen des naturhistorischen Vereins der preussischen Rheinlande und Westfalens.
Verh. Physiol. Ges. Berlin .	Verhandlungen der Physiologischen Gesellschaft zu Berlin.
Verh. Schweiz. Nat. Ges. . .	Verhandlungen der Schweizerischen Naturforschenden Gesellschaft, Basel.
Vict. Mem. Mus. Geol. Survey, Canada.	Victoria Memorial Museum Geological Survey of Canada, Bulletin.
Videnskab. Skrifter . . .	Skrifter udgivne af Videnskabsselskabet i Kristiania.
Wiener Klin. Woch. . . .	Wiener Klinische Wochenschrift.
Wiss. Abhandl. Physikal.-Tech. Reichsanst.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Wochbl. Papierfabr. . . .	Wochenblatt für Papierfabrikation.
Woch. f. Brau. . . . .	Wochenschrift für Brauerei.
Zeitsch. allg. Physiol. . .	Zeitschrift für allgemeine Physiologie.
*Zeitsch. anal. Chem. . .	Zeitschrift für analytische Chemie.
*Zeitsch. angew. Chem. . .	Zeitschrift für angewandte Chemie.
*Zeitsch. anorg. Chem. . .	Zeitschrift für anorganische und allgemeine Chemie.
Zeitsch. Biol. . . . .	Zeitschrift für Biologie.
Zeitsch. deut. Geol. Ges. .	Zeitschrift der deutschen Geologischen Gesellschaft.
*Zeitsch. Elektrochem. . .	Zeitschrift für Elektrochemie.
Zeitsch. exp. Path. Ther. .	Zeitschrift für experimentelle Pathologie und Therapie.

ABBREVIATED TITLE.	JOURNAL.
Z. ges. Brauw. . . . .	Zeitschrift für das gesammte Brauwesen.
<i>Zeitsch. ges. exp. Med.</i> . . .	Zeitschrift für die gesamte experimentelle Medizin.
Z. ges. Schiess- u. Sprengstoffw. . . . .	Zeitschrift für das gesammte Schiess- und Sprengstoffwesen.
<i>Zeitsch. Hyg.</i> . . . . .	Zeitschrift für Hygiene und Infektionskrankheiten.
<i>Zeitsch. Immunit.</i> . . . . .	Zeitschrift für Immunitätsforschung und experimentelle Therapie.
<i>Zeitsch. Instrument.</i> . . . .	Zeitschrift für Instrumentenkunde.
<i>Zeitsch. Kryst. Min.</i> . . . .	Zeitschrift für Krystallographie und Mineralogie.
Z. öffentl. Chem. . . . .	Zeitschrift für öffentliche Chemie.
* <i>Zeitsch. physikal. Chem.</i> . .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandschaftslehre.
<i>Zeitsch. physikal. Chem. Unterr.</i> . . . . .	Zeitschrift für den physikalischen und Chemischen Unterricht.
<i>Zeitsch. physiol. Chem.</i> . . .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
<i>Zeitsch. prakt. Geol.</i> . . . .	Zeitschrift für praktische Geologie.
* <i>Zeitsch. Sauerstoff Stickstoff Ind.</i> . . . . .	Zeitschrift für Sauerstoff und Stickstoff Industrie.
Z. Spiritusind. . . . .	Zeitschrift für Spiritusindustrie.
Z. Unters. Nahr. Genussm. . . . .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Z. Ver. deut. Zuckerind. . . . .	Zeitschrift des Vereins der deutschen Zucker-Industrie.
<i>Zeitsch. wiss. Mikrosk.</i> . . .	Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik.
* <i>Zeitsch. wiss. Photochem.</i> . .	Zeitschrift für wissenschaftliche Photographie, Photo-physik und Photochemie.
* <i>Zeitsch. Zuckerind. Cecho-slov.</i> . . . . .	Zeitschrift für Zuckerindustrie der Čechoslovakischen Republik.

# JOURNAL OF THE CHEMICAL SOCIETY.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

## PART I.

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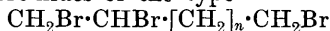
### Organic Chemistry.

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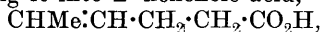
**Thermal Expansion of [Solid] Paraffin and Solutions of [Solid] Paraffin.** W. VON PIOTROWSKI (*Zeitsch. physikal. Chem.*, 1919, **93**, 596—606).—The specific gravity of nine specimens of solid paraffin, from naphtha, with varying points of solidification ( $50.5$ — $64.0^{\circ}$ ), has been determined at temperatures between  $18^{\circ}$  and  $67^{\circ}$ , and the results compared with those found by Ziętkowski for the paraffin obtained from lignite tar (*Diss.*, Freiberg, 1900). It is found that the coefficient of expansion of solid naphtha paraffin lies between  $0.000842$  and  $0.005108$ . Lignite paraffin when melted has a coefficient of expansion about twice as large as that of naphtha paraffin, but for the two solids the values are about the same. The dependence of the specific gravity of solutions on the temperature in the case of solvents of high specific gravity may be expressed by an equation based on the mixture law. In the case of solvents of low specific gravity, irregularities are found in the neighbourhood of the melting point. The specific gravity of solutions at temperatures above the melting point of the paraffin may be approximately calculated by the mixture law. J. F. S.

**Low Temperature Carbonisation.** TERN (*Ber.*, 1919, **52**, [B], 1836).—The principles of the process described by Fischer and Gluud (*A.*, 1919, i, 377) were first applied by the author on the factory scale in 1910. J. C. W.

**$\alpha\gamma\delta$ -Tribromopentane from  $\alpha\epsilon$ -Dibromopentane.** JULIUS VON BRAUN and GEORG KIRSCHBAUM. (*Ber.*, 1919, **52**, [B], 1713—1716).—Tribromides of the type



react with magnesium to form Grignard compounds of the formula  $\text{CH}_2\text{:CH}\cdot[\text{CH}_2]_n\cdot\text{CH}_2\cdot\text{MgBr}$ , which may be converted into iodides,  $-\text{CH}_2\text{I}$ , by means of iodoacetonitrile (see A., 1912, i, 434). From the magnesium compound or the iodide it would be possible to synthesise substances containing unsaturated alkyl groups, and consequently the authors have sought for methods whereby the tribromides of the desired type might be prepared conveniently, and have found the most promising material to be the  $\alpha\omega$ -dibromoparaffins. These only react with bromine in the presence of iron wire, and then the reaction is vigorous and so much bromine is lost that the process must be repeated. The position of the bromine atoms in the product is not what might be expected. In the case of  $\alpha\epsilon$ -dibromopentane, for example, the product is  $\alpha\gamma\delta$ -tribromopentane,  $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CH}_3$ , a stable oil with spicy odour, b. p. 120—124°/11 mm., and not the expected  $\alpha\delta\epsilon$ -compound, b. p. 128—132°/12 mm. (A., 1918, i, 164). Its constitution is proved by converting it into  $\Delta^7$ -hexenoic acid,



through the Grignard reaction.

J. C. W.

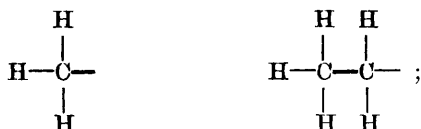
**Method of Producing Methyl Alcohol from Alkyl Formates.** J. A. CHRISTIANSEN (U.S. Pat. 1302011).—Methyl alcohol is produced by treating an alkyl formate with hydrogen in the presence of a catalyst, for example, partly reduced copper at 180°,  $\text{H}\cdot\text{CO}_2\text{Me} + 2\text{H}_2 = 2\text{MeOH}$ . The methyl formate may be produced by leading carbon monoxide and methyl alcohol vapour, at high pressure, over solid sodium methoxide, or by passing carbon monoxide into a solution of sodium methoxide in methyl alcohol,  $\text{CO} + \text{Me}\cdot\text{OH} = \text{H}\cdot\text{CO}_2\text{Me}$ .

**The Distillation of Aqueous Solutions of Ethylene Monochlorohydrin.** J. BANCELIN and G. RIVAT (*Bull. Soc. chim.*, 1919, [iv], **25**, 552—560).—The distillation of commercial aqueous solutions of ethylene monochlorohydrin gives a distillate passing at a fixed point (97.85°/760 mm.) containing 42% of the monochlorohydrin, independent of the concentration of the original solution. These results are confirmed by figures obtained with solutions made from the pure monochlorohydrin, except that in this case the distillate has a content of 41% of monochlorohydrin. Such a distillate has  $D^{15}_4$  1.094. There is no direct evidence of the formation of a hydrate.

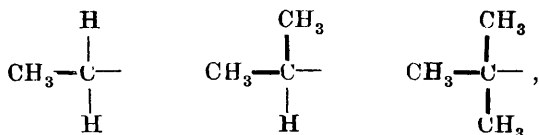
W. G.

**Pinacolin Transformations. V. The Varying Affinity Demands of Aliphatic Radicles.** HANS MERRWEIN (*Annalen*, 1919, **419**, 121—175).—It has been shown that the pinacolin transformation is caused by the direct loss of a hydrogen atom and a hydroxyl group from the molecule of the glycol, and subsequent

migration of a radicle. With symmetrical glycols, it is a matter of indifference as to which hydroxyl group is eliminated, but with unsymmetrical glycols of the type  $\text{OH}\cdot\text{CR}_2\cdot\text{CR}_2'\cdot\text{OH}$ , two distinct products,  $\text{CR}_2\text{R}'\cdot\text{CO}\cdot\text{R}'$  and  $\text{CRR}_2'\cdot\text{CO}\cdot\text{R}$ , result, according as the one or the other hydroxyl group is expelled. In general, the less firmly attached group will be mainly or entirely eliminated, and the nature of the pinacolin produced therefore throws considerable light on the relative strength of the attachment of the hydroxyl groups. Since, however, these may be regarded as being bound by the residue of the affinity of the carbon atom which is not required by the alkyl groups, a direct method of comparing the affinity demands of various alkyl groups is provided. A series of comparisons by this method is described in the present communication. It is found that the valency requirements of the normal alkyl groups diminish with increasing number of carbon atoms; this diminution, however, is not continuous, but exhibits a periodicity of such nature that the alkyl groups with an odd number of carbon atoms have greater affinity demands than those with an even number of carbon atoms. This apparent anomaly is, however, readily explained when the groups are formulated in the following manner, in which the light and heavy strokes represent the different affinity demands:



if, now, the *n*-propyl group is considered as formed by the displacement of a hydrogen atom in methyl by the ethyl radicle, it is seen that it must have a greater valency requirement than the ethyl group, since the demand of the latter is less than that of the methyl group. By a similar line of reasoning, it is seen that the affinity requirement must diminish uniformly in the case of alkyl groups with side-chains



and this appears to be the case as far as the evidence available allows conclusions to be drawn.

[With ADOLF SCHWEINHEIM.]—The action of magnesium *n*-propyl bromide on methyl dimethylglycolate (compare Parry, T., 1911, **99**, 1171) leads to the formation of a mixture of *as*-dimethyldi-*n*-propylethylene glycol and dimethyl-*n*-propylethylene glycol, the Grignard compound behaving in part as a reducing agent and evolving propylene. The b. p.'s of the constituents lie so closely together that the substances cannot be separated by fractionation,



and the mixture was therefore submitted to the action of ice-cold concentrated sulphuric acid, whereby propyl isopropyl ketone, b. p. 135—136° (semicarbazone, m. p. 119°), and a mixture of the theoretically possible pinacolins were obtained. The latter are conveniently separated and approximately estimated by taking advantage of the great differences in the readiness with which they react with semicarbazide and the widely differing solubilities of the semicarbazones. *aa-Methyldi-n-propylacetone* [*methyl α-methyl-α-propylbutyl ketone*],  $\text{CMePr}_2 \cdot \text{COMe}$ , is an oil with a pronounced camphoraceous odour, b. p. 191·5—192°,  $D_4^{20}$  0·8351,  $n_D^{20}$  1·42927 (semicarbazone, coarse needles, m. p. 149—150°), whilst *n-propyl αα-dimethylbutyl ketone*,  $\text{CMe}_2\text{Pr} \cdot \text{COPr}$ , has b. p. 188·5—189°,  $D_4^{20}$  0·8295,  $n_D^{20}$  1·42634 (semicarbazone, slender needles, m. p. 104°). The ratio of the amounts of the latter to the former in the mixture is 10:8. A similar ratio (11:8) was obtained by oxidising the mixture with boiling dilute nitric acid and separating the acids formed; in this manner, *αα*-dimethylvaleric acid, b. p. 105—108°/14 mm., and *α-methyl-α-n-propylvaleric acid*, b. p. 118—122°/14 mm., m. p. 43—44°, were obtained. A mixture of *dimethylmonobutylethylene glycol* [*β-methylheptane-β-γ-diol*], b. p. 109—113°/10·5 mm., and *as-dimethyldi-n-butylethylene glycol* [*β-methyl-γ-butylheptane-β-γ-diol*], m. p. 32—32·5°, b. p. 130·5—131°/9 mm., was prepared from magnesium *n*-butyl bromide and dimethylglycollic ester; the latter glycol yielded a mixture of pinacolins, which could be separated and approximately analysed by means of semicarbazide. *Methyl-αα-di-n-butylacetone* [*γ-methyl-γ-butylheptane-β-one*] forms a colourless oil with a peculiar, sweet odour, b. p. 107·5—108·5°/14 mm.,  $D_4^{20}$  0·8380,  $n_D^{20}$  1·43667 (semicarbazone, coarse needles, m. p. 108°), the constitution of which is deduced by its oxidation with dilute nitric acid to *α-methyl-α-n-butylvaleric acid*, a viscous oil, b. p. 158—159°/18 mm. *n-Butyl tert.-heptyl ketone* [*εε-dimethyldecane-ζ-one*] is a colourless, mobile oil, b. p. 105·5—106·5°/15 mm.,  $D_4^{20}$  0·8323,  $n_D^{20}$  1·43420, and is transformed by nitric acid into *αα-dimethylvaleric acid*, b. p. 120—122°/15 mm. The ratio of butyl *tert.*-heptyl ketone to methyldibutylacetone in the pinacolin mixture is approximately 7:4.

The investigation has been extended to tetraethylethylene glycol, since, according to Kohn (A., 1905, i, 928) and Samec (A., 1907, i, 746), this substance does not yield a true pinacolin, but an isomeric alkylene oxide. This supposition is based on the facts that it does not yield an oxime and is indifferent towards zinc ethyl. It is now shown however, that the glycol actually yields ethyl *tert.*-heptyl ketone [*γγ*-diethylhexane-δ-one], b. p. 194—195°,  $D_4^{20}$  0·8501,  $n_D^{20}$  1·43519, as is shown by the formation of *αα*-diethylbutyric acid, m. p. 38°, b. p. 121—122°/16 mm.,  $D_4^{40\cdot3}$  0·9119,  $n_D^{40\cdot3}$  1·42778 (sodium salt, leaflets,  $+3\text{H}_2\text{O}$ ), when the latter is oxidised with dilute nitric acid.

The relative firmness of attachment of the methyl and ethyl groups is further demonstrated in the behaviour of *αα*-diphenyl-

*ββ-methylethylethylene glycol* [*αα-diphenyl-β-methylbutane-αβ-diol*], which is obtained as a colourless, very viscous oil, b. p. 202°/12 mm., by the action of magnesium phenyl bromide on methyl methylethylglycolate. The glycol is transformed by concentrated sulphuric acid exclusively into *αα-diphenyl-α-ethylacetone* [*γγ-diphenylpentane-δ-one*], coarse leaflets, m. p. 27°, b. p. 179°/11 mm. (*semicarbazone*, slender needles, m. p. 199—200°), the constitution of which is deduced from its conversion by sodium hypobromite into *αα-diphenylbutyric acid*, m. p. 172—173·5°, and from its transformation by soda-lime into *αα-diphenylpropane*, b. p. 274—280°, and acetic acid.

[With FRITZ KREMERS.]—As in previous cases, the action of magnesium *n*-propyl bromide on methyl 1-cyclopentanol-1-carboxylate gave rise to a mixture of "*propyltetramethyleneglycol*"

[1-*α-hydroxybutylcyclopentan-1-ol*],  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{C}(\text{OH}) \cdot \text{CHPr} \cdot \text{OH}$ ,

and "*as-di-n-propyltetramethyleneglycol*" [1-*α-hydroxy-α-propylbutylcyclopentan-1-ol*],  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{C}(\text{OH}) \cdot \text{CPr}_2 \cdot \text{OH}$ , which could

not be separated satisfactorily by fractional distillation, and was therefore immediately submitted to the dehydrating action of aqueous oxalic or concentrated sulphuric acids, the products of which were *butyrylcyclopentane*, colourless oil, b. p. 198° (*oxime*, colourless oil, b. p. 135—138°/21 mm., *semicarbazone*, slender needles, m. p. 110—111°), and a mixture of pinacolins, which were separated through their *semicarbazones*. 1:1-*Dipropylcyclohexan-2-one* is a colourless oil with an intense odour of peppermint, b. p. 119—120°/17 mm.,  $D_4^{20}$  0·9062,  $n_D^{20}$  1·46172 (*semicarbazone*, slender needles grouped in rosettes or large, transparent, apparently monoclinic prisms, m. p. 182°), which is not readily oxidised by nitric acid to *αα-dipropyladipic acid*; that the acid is actually formed, however, could be shown by converting the product of oxidation into its dimethyl ester (b. p. 158—160°/18 mm.), transforming the latter into methyl dipropylcyclopentanonecarboxylate, and further into 2:2-dipropylcyclopentanone (A., 1913, i, 485), the *semicarbazone* of which had m. p. 211°. 1-*Butyryl-1-propylcyclopentane* forms a colourless, volatile oil with an odour of peppermint, b. p. 115—117°/18 mm.,  $D_4^{20}$  0·8952,  $n_D^{20}$  1·45544 (*semicarbazone*, m. p. 116°), the constitution of which follows from its smooth oxidation to 1-*propylcyclopentane-1-carboxylic acid*, colourless needles, m. p. 7°, b. p. 142°/18 mm.

The action of magnesium ethyl bromide on methyl cyclohexan-1-ol-1-carboxylate (b. p. 96°/16 mm.) yielded a mixture of "*as-diethylpentamethylene glycol*" [1-*α-hydroxy-α-ethylpropylcyclohexan-1-ol*] and "*ethylpentamethylene glycol*" [1-*α-hydroxypropylcyclohexan-1-ol*], which could be incompletely separated, since the latter gradually crystallised in needles, m. p. 61—63°. The yield of pinacolin was unusually poor, and separation of the mixture of ketones was readily effected, since only the propionylcyclohexanone (formed by loss of water from the residual "*ethylpentamethylene*"

glycol"), colourless oil with the odour of amyl acetate, b. p.  $196^{\circ}$ /atmospheric pressure,  $88-89^{\circ}/19$  mm.,  $D_4^{20}$  0.9105,  $n_D^{20}$  1.45304 (semicarbazone, shining leaflets, m. p.  $150-152^{\circ}$ ), proved capable of forming an oxime, four-sided plates, m. p.  $70-72^{\circ}$ . The portion which did not react with hydroxylamine consisted solely of 1-propionyl-1-ethylcyclohexane, colourless oil with the odour of peppermint, b. p.  $109-111^{\circ}/21$  mm.,  $D_4^{20}$  0.9178,  $n_D^{20}$  1.46292, the constitution of which follows from its unusually smooth oxidation to 1-ethylcyclohexane-1-carboxylic acid, m. p.  $39-40^{\circ}$ , b. p.  $140^{\circ}/15$  mm.

It has been shown previously (A., 1913, i, 485) that hydroxy-benzhydrylcyclohexanol passes by loss of water into a so-called  $\alpha$ -pinacolin, the corresponding oxide; it has now been found possible to convert the latter into the true  $\beta$ -pinacolin, 1-benzoyl-1-phenylcyclohexane, prisms, m. p.  $73-74^{\circ}$ , the constitution of which is deduced from its smooth fission by fusion with potassium hydroxide into phenylcyclohexane, m. p.  $7^{\circ}$ , b. p.  $235-236^{\circ}$ , and benzoic acid.

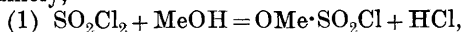
H. W.

### Catalytic Preparation by the Dry Way of Ethyl Ether.

A. MAILHE and F. DE GODON (*Bull. Soc. chim.*, 1919, [iv], 25, 565-568).—Aluminium oxide, as the catalyst, was prepared by heating commercial alum to  $190-195^{\circ}$ . Using a suitable amount of catalyst, disposed in four units, and heated in each case to  $190-195^{\circ}$ , a yield of ethyl ether equivalent to 71.3% of the theory was obtained when using 95% alcohol. The yield depends rather on the weight of the catalyst employed than on the surface exposed. It is also dependent on the concentration of the alcohol used.

W. G.

**Action of Methyl Alcohol on Sulphuryl Chloride and on Methyl Chlorosulphonate.** R. LEVAILLANT and L. J. SIMON (*Compt. rend.*, 1919, 169, 854-857).—The action of methyl alcohol on sulphuryl chloride may be considered as occurring in two stages, namely,



Another reaction, more important than that represented in (2), occurs, however,  $\text{OMe} \cdot \text{SO}_2\text{Cl} + \text{MeOH} = \text{MeHSO}_4 + \text{MeCl}$ . There are other secondary reactions, such as that of the hydrogen chloride and methyl alcohol with production of methyl chloride and water, which may affect the ultimate results of all the changes. The methyl hydrogen sulphate formed according to the third equation decomposes on distillation, giving methyl sulphate and sulphuric acid. By suitably modifying the conditions, a good yield of methyl chlorosulphonate may be obtained. [See, further, *J. Soc. Chem. Ind.*, 1919, 962A.]

W. G.

**Preparation and Physical Properties of Dinitroglycol [Ethylene Dinitrate].** I. and II. ANNIBALE MORESCHI (*Atti R. Accad. Lincei*, 1919, [v], 28, i, 393-397, 428-431).—Ethylene

dinitrate has been prepared according to the scheme: ethylene  $\rightarrow$  ethylene dibromide  $\rightarrow$  ethylene diacetate  $\rightarrow$  ethylene glycol  $\rightarrow$  ethylene dinitrate, the ethylene used being obtained in 96% yield by passing alcohol vapour over alumina heated at  $350\text{--}360^\circ$ , and the nitration of the glycol effected by means of a mixture of sulphuric and nitric acids. The specific gravities of ethylene dinitrate at  $t^\circ/4^\circ$  vary rectilinearly with the temperature, and between  $0^\circ$  and  $41.5^\circ$  are given by the expression

$$1.4883[1 - 0.000775(t - 15)];$$

the corresponding expression for glyceryl trinitrate between  $0^\circ$  and  $55.5^\circ$  is  $1.5984[1 - 0.0008577(t - 15)]$ . The surface tension is also a linear function of the temperature: for ethylene nitrate,  $4.76(1 - 0.0021t)$ , and for glyceryl trinitrate,  $5.18(1 - 0.003t)$ . The viscosity of glyceryl trinitrate is far greater, and below  $20^\circ$  increases far more rapidly with fall of temperature, than that of ethylene dinitrate. The vapour tension of ethylene dinitrate at  $20^\circ$  is 0.3 mm.

The properties are given of various explosive products obtained by mixing ethylene dinitrate and glyceryl trinitrate with cellulose nitrate.

T. H. P.

### Reciprocal Influence of the Fatty Acids on the Solubility.

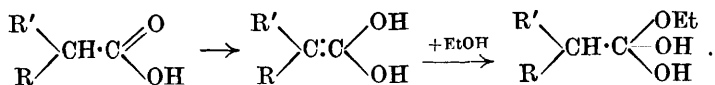
P. WAENTIG and G. PESCHECK (*Zeitsch. physikal. Chem.*, 1919, **93**, 529—569).—The solubility of a fatty acid in certain solvents is often very much increased by the presence of a second fatty acid. The increase is always reciprocal and often very considerable. For example, the solubility of palmitic acid in carbon tetrachloride is increased 250% by the presence of lauric acid. The increase in solubility decreases with increase of the disturbing acid and approaches a limiting value. An attempt is made to explain the increased solubility by the formation of readily soluble compounds of the two acids, but a direct proof could not be obtained, for molecular weight determinations, both by the ebullioscopic and cryoscopic methods, of one fatty acid in the presence of a second gave no difference in the boiling point or freezing point from that obtained with the pure solvent. But since the fatty acids are bimolecular in the solvents in which the increase of solubility is observed, this does not disprove the absence of compounds, for such compounds could well be formed without any change occurring in the number of molecules present, thus:  $L_2 + P_2 = 2LP$ . If the view is correct, the formation of compounds, and also the increase in solubility, should not take place in those solvents in which the acids are unimolecular. It is found that in carbon tetrachloride, chloroform, benzene, toluene, and nitrobenzene solutions, in which the fatty acids are bimolecular, the increase in solubility occurs, but in ethyl alcohol, ethyl ether, ethyl acetate, and benzaldehyde solutions, in which the fatty acids are unimolecular, the increase in solubility is not observed. It is also found that the increase in solubility is not restricted to the fatty acids, but occurs also with aromatic acids, and in a much smaller degree with ketones and alcohols, so that it is suggested that the subsidiary valencies of the

carbonyl oxygen are responsible for the effect. A determination of the influence of temperature on the increase of solubility indicates that temperature has practically no effect on the increase. It is also shown that temperature has no influence on the association of the fatty acids in solution. The solubility of palmitic acid is influenced by the quantity of undissolved acid, and also to a very marked extent by traces of moisture. During the purification of palmitic acid, it was found that the solubility in a stated volume of a given solvent furnished a much better criterion of the purity of the acid than did the melting point. The density and vapour tension of liquid mixtures of fatty acids were determined, and it is shown that the values are not in keeping with the mixture law, from which it is deduced that compounds of the two acids are present in the fused mass. From the fusion curve of mixtures of palmitic and lauric acids, it is shown that an equimolecular compound of the two acids exists in the solid state. J. F. S.

**Preparation of Chloromethyl Chloroformates.** ANDRÉ KLING, D. FLORENTIN, A. LASSIEUR, and R. SCHMUTZ (*Compt. rend.*, 1919, **169**, 1046—1047).—Carbonyl chloride condenses with methyl alcohol to give methyl chloroformate, which when acted on by chlorine in sunlight gives chloromethyl chloroformate, then dichloromethyl chloroformate, and finally the trichloromethyl ester. It is almost impossible to separate the first two esters by fractional distillation, but the dichloro- and trichloro-derivatives can be separated in this way. An alternative method is to chlorinate methyl formate in sunlight, but in this case some dichloromethyl formate is obtained. W. G.

**Anomalies in the Formation of Esters from Acids and Alcohols.** E. PREISWERK (*Helv. Chim. Acta*, 1919, **2**, 647—654).—Diethylmalonic acid cannot be esterified by alcohol and sulphuric acid or hydrogen chloride, the only ester which can be isolated being ethyl  $\alpha$ -ethylpropionate in small quantity. Under similar conditions, ethyl malonate is formed in good yield from malonic acid.

A critical review of the literature on esterification leads the author to the conclusion that it is primarily an additive process. In general, however, there is but little tendency for the carbonyl portion of the carboxyl group to form additive compounds unless it is influenced by the presence of a neighbouring carbonyl group (as in oxalic or pyruvic acids) or by the tendency towards enolisation of a hydrogen atom in the  $\alpha$ -position:



Esterification, according to this hypothesis, should occur most readily with acids containing a mobile  $\alpha$ -substituted hydrogen atom, and this appears to be the case when, for example, chloroacetic, cyanoacetic, and phenylacetic acids are compared with acetic

acid. As usually formulated, benzoic acid does not contain a hydrogen atom in the  $\alpha$ -position, and yet it is readily esterified; the author seeks an explanation of the apparent anomaly in the oscillation hypothesis, which postulates the presence of the hydrogen atom in this position during the half-interval of time. The catalytic acceleration of esterification by mineral acids is attributed to the suppression of the ionisation of the organic acid, and consequent increase in the enolisation.

H. W.

**Some Ternary Systems containing Alkali Oxalates and Water.** ALBERT CHERBURY DAVID RIVETT and EDMUND ARTHUR O'CONNOR (T., 1919, 115, 1346—1354).

**Preparation of Maleic Acid.** JOHN M. WEISS and CHARLES R. DOWNS (U.S. Pat. 1318632).—A mixture of benzene and benzoquinone in the vapour phase is oxidised by treatment under pressure with a gas containing oxygen at a temperature of 300—700° in the presence of vanadium oxide. The maleic acid produced is separated, and the residual, unchanged benzene and benzoquinone are again subjected to the same treatment.

G. F. M.

**Slow, Partial Change of an Aqueous Solution of Maleic Acid into Fumaric Acid at the Ordinary Temperature and in the Absence of Light.** ANTON KAILAN (*Zeitsch. physikal. Chem.*, 1919, 93, 613—616).—From electro-conductivity measurements with a solution of maleic acid which had been kept in the dark for five years, it is shown that about 4% of the acid had become changed into fumaric acid.

J. F. S.

**Various Bismuth Compounds.** L. VANINO and F. MUSSGNOG (*Arch. Pharm.*, 1919, 257, 267—269).—The following bismuth salts have been prepared with the help of bismuth-mannitol solution, obtained by grinding together crystalline bismuth nitrate (1 mol.) and mannitol (1 mol.) and treating the mass with water.

*Bismuth anhydromethylenecitrate*,  $\text{Bi}_2(\text{C}_7\text{H}_6\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$ , prepared from the corresponding sodium salt ("citarine") and bismuth-mannitol, forms an odourless, white, granular powder, and is reduced to metallic bismuth when heated with alkali hydroxide.

*Bismuth diethylmalonate*,  $\text{Bi}_2(\text{C}_7\text{H}_{10}\text{O}_4)_3$ , is obtained as a voluminous, white precipitate from the sodium salt and bismuth-mannitol solution.

*Bismuth mandelate*,  $\text{Bi}(\text{C}_8\text{H}_7\text{O}_3)_3$ , prepared from mandelic acid and bismuth-mannitol solution, forms a white, indistinctly crystalline precipitate, m. p. 210—215° (decomp.).

*Bismuth vanillate*,  $\text{Bi}(\text{C}_8\text{H}_7\text{O}_4)_3 \cdot 2\text{H}_2\text{O}$ , obtained from the sodium salt and bismuth-mannitol solution, forms yellowish-white, nodular crystals with no sharp melting point.

*Bismuth cinnamate*,  $\text{Bi}(\text{C}_9\text{H}_7\text{O}_2)_3 \cdot 3\text{H}_2\text{O}$ , forms nodular crystals with an indistinct melting point.

Bismuth acetate may be prepared in 95% yield by heating bismuth

oxide or hydroxide in a reflux apparatus with acetic anhydride, its formation being accelerated by the presence of a little glacial acetic acid.

T. H. P.

**Preparation of Formaldehyde from Formates.** H. and S. (*Caoutchouc et Guttapercha*, 1919, 16, 9803; from *Chem. Zentr.*, 1919, iv, 412).—Formaldehyde is produced when metallic formates are heated, the necessary temperature increasing with increase in the basic properties of the metal. The optimum temperatures are as follows: Cu, 170°; Pb, 195—200°; Ni, 210°; Zn, 240°; Fe, 245°; Mn, 295°; Ba, 325°; Ca, 335°; Mg, 340°; Sr, 355°; Na, 355°; K, 375°. A large portion of the formaldehyde is immediately transformed into methyl alcohol and formic acid. Methyl alcohol and formaldehyde are produced when formic acid is passed at the high temperature over zinc oxide or thorium oxide.

H. W.

**Diastase-like Properties of Formaldehyde. Action of Formaldehyde on Starch.** HARRY MAGGI (*Fermentforsch.*, 1919, 2, 304—447; from *Chem. Zentr.*, 1919, iii, 635).—The main results obtained in the investigations have already been reported by Woker. The apparent degradation of starch appears to proceed most readily in faintly acid solution. Experiments are now recorded on the action of mixtures of formaldehyde or saliva with glycogen solution and iodine and on the precipitation of starch or glycogen by formaldehyde. The latter phenomenon is also observed with formic or other acids. A method of estimating diastase, based on the alteration in shade in the mixtures described above, could not be worked out in consequence of this action.

H. W.

**The Diastase-like Properties of Formaldehyde.** G. WOKER and H. MAGGI (*Ber.*, 1919, 52, [B], 1594—1604).—The authors reiterate their arguments in favour of the view that formaldehyde acts on starch in a certain measure like diastase, and reply to recent criticisms (*A.*, 1919, i, 253, 311, 312). They hold the view that under the prolonged influence of formaldehyde the primary hydrolytic products are rebuilt into non-hydrolysable and non-reducing substances, such as the so-called "reversion dextrin," and in this way they meet most of the criticism, for the authors, in their desire to give the hydrolysis every assistance of time and temperature, did just the reverse by generally keeping the mixtures of starch and formaldehyde too long. A similar rebuilding of hydrolytic products is known to occur when egg albumen is digested with papain (see Abderhalden's book).

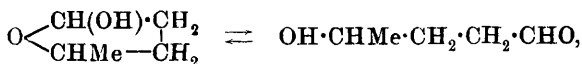
J. C. W.

**The Stabilisation of Acraldehyde. III. Preparation of Acraldehyde.** CHARLES MOUREU and ADOLPHE LÉPAPE (*Compt. rend.*, 1919, 169, 885—889).—For the preparation of acraldehyde from glycerol the authors recommend the use of a mixture of 5 parts of potassium hydrogen sulphate with 1 part of potassium sulphate as a dehydrating agent. Using such a mixture, to which is added one-quarter of its weight of glycerol, the heating being

carefully controlled and the glycerol replaced as exhausted, they obtained a yield of pure acraldehyde equivalent to 67.5% of the theoretical yield. [See, further, *J. Soc. Chem. Ind.*, 1920, 42A.]

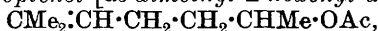
W. G.

**$\gamma$ -Hydroxyaldehydes. II.** BURCKHARDT HELFERICH (*Ber.*, 1919, 52, [B], 1800—1812. Compare A., 1919, i, 386).—In the former paper it was shown that  $\gamma$ -hydroxyvaleraldehyde behaves like a furan derivative, and yields an acetate and a methyl compound of the same type. Starting with methylheptenol, this has now been acetylated and methylated, the derivatives ozonised in glacial acetic acid, and then treated with zinc dust, giving the acetate and methyl ether of the normal form of  $\gamma$ -hydroxyvaleraldehyde. The isomerides differ in molecular refraction and chemical properties in the expected manner. Apparently, the free  $\gamma$ -hydroxyvaleraldehyde, or rather 2-hydroxy-5-methyltetrahydrofuran, is desmotropic with the true aldehyde form, thus:



which may be demonstrated as follows: by adding equal quantities of Schiff's reagent or ammoniacal silver oxide to equivalent solutions of " $\gamma$ -hydroxyvaleraldehyde" (1%),  $\gamma$ -methoxyvaleraldehyde and acetaldehyde (0.44%), the characteristic reactions are complete in a few seconds with the true aldehydes, but develop gradually with the furan derivative. Similar phenomena are exhibited by  $\gamma$ -hydroxyhexaldehyde.

*Acetylmethylheptenol* [*ac*-dimethyl- $\Delta$ -hexenyl acetate],



from methylheptenol and acetic anhydride, has b. p. 78—78.5°/9 mm.,  $D_4^{17.9}$  0.8928,  $n_D^{17.9}$  1.4328, and *methylheptenol methyl ether* [ *$\beta$* -methoxy- $\zeta$ -methyl- $\Delta^6$ -heptene], from methylheptenol, sodium, and methyl iodide, has b. p. 50—50.5°/9 mm., 163.5°/752 mm. (corr.),  $D_4^{18}$  0.8103,  $n_D^{18}$  1.4281.  *$\gamma$ -Acetoxyvaleraldehyde* has b. p. 88—91°/12 mm.,  $D_4^{18}$  1.011,  $n_D^{18}$  1.4226, and is very sparingly soluble in water.  *$\gamma$ -Methoxyvaleraldehyde*,  $\text{OMe·CHMe·CH}_2\text{·CH}_2\text{·CHO}$ , is a limpid, mobile liquid, soluble in water (1 in 5), b. p. 43—44°/10 mm.,  $D_4^{18}$  0.9161,  $n_D^{18}$  1.4134.

Whereas the furan derivative is merely converted into its methyl ether, 2-methoxy-5-methyltetrahydrofuran, under the influence of methyl-alcoholic hydrogen chloride, the true  $\gamma$ -methoxyvaleraldehyde, like aldol (prepared by Grignard's method, A., 1907, i, 287), gives a dimethylacetal.  *$\alpha\alpha\delta$ -Trimethoxy-pentane*, from methoxyvaleraldehyde, is a very soluble liquid with a burning taste, b. p. 72°/12 mm.,  $D_4^{18}$  0.9197,  $n_D^{18}$  1.4119, and  *$\alpha\alpha$ -dimethoxybutan- $\gamma$ -ol*, from aldol, has b. p. 71—76°/9 mm.,  $D_4^{18}$  0.9894,  $n_D^{18}$  1.4200.

Just as aldol may be converted into pentan- $\beta\delta$ -diol by means of magnesium methyl iodide, so  $\gamma$ -methoxyvaleraldehyde yields  *$\epsilon$ -methoxyhexan- $\beta$ -ol*,  $\text{OH·CHMe·CH}_2\text{·CH}_2\text{·CHMe·OMe}$ , b. p. 79—80°/9 mm.,  $D^{18}$  0.9048,  $n_D^{18}$  1.4263. Similarly, if the free



" $\gamma$ -hydroxyvaleraldehyde" were a true aldehyde it would form the known hexane- $\beta\epsilon$ -diol, but whilst it reacts to form methane, the intermediate magnesium compound regenerates the original substance and complex products on decomposition with dilute sulphuric acid.

$\Delta^7$ -Pentenoyl chloride is slowly added to well-chilled zinc ethyl and the product is decomposed by ice giving *ethyl  $\Delta^7$ -butenyl ketone*,  $\text{CH}_3\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COEt}$ , b. p.  $46\text{--}47^\circ/12$  mm.,  $D_4^{18.3}$  0.8487,  $n_D^{18.3}$  1.4254, an unpleasant-smelling liquid, which forms a *semicarbazone*, thin, rhombic plates, m. p.  $82\text{--}83^\circ$  (corr.), and is reduced by sodium and alcohol to  *$\Delta^8$ -hepten- $\epsilon$ -ol*, b. p.  $60\text{--}61.5^\circ/11$  mm.,  $D_4^{18}$  0.8447,  $n_D^{18}$  1.4369. This is ozonised as above, and thus converted into  *$\gamma$ -hydroxyhexaldehyde* [or, rather, the desmotrope, *5-hydroxy-2-ethyltetrahydrofuran*], a fairly mobile, limpid liquid, b. p.  $77\text{--}80^\circ/11$  mm.,  $D_4^{18}$  1.004,  $n_D^{18}$  1.4398, which condenses with methyl alcohol to form the half-acetal, that is, *5-methoxy-2-ethyltetrahydrofuran*, b. p.  $139\text{--}145^\circ/760$  mm. (corr.),  $D_4^{18}$  0.9225,  $n_D^{18}$  1.4164, a mobile oil with odour reminiscent of peppermint. J. C. W.

**Manufacture of Acetone and Carbon Dioxide.** SOCIÉTÉ ANONYME DES ACIERIES & FORGES DE FIRMINY (Brit. Pat., 134144).—Acetic acid of 90—100% strength is catalysed over manganese peroxides prepared either by precipitation or by crushing and screening natural pyrolusite, pieces of a diameter of 5—7 mm. being employed. Catalysis occurs without appreciable subsidiary reaction between wide limits of temperature, for instance,  $350\text{--}450^\circ$ . The catalyst is packed in a cylinder and heated either externally or, preferably, by mixing with  $1\text{--}1\frac{1}{2}$  volumes of crushed coke similarly screened, and passing an electric current through the mixture by means of two iron or aluminium electrodes. The acetone produced is separated from the carbon dioxide by condensation, and scrubbing in water-sprinkling towers. The catalyst is much more stable than Sabatier's manganous oxide, and when the activity does decline, it is only necessary to heat it in a current of air to revivify it.

G. F. M.

**The Production of Methyl Ethyl Ketone from *n*-Butyl Alcohol.** ALBERT THEODORE KING (T., 1919, 115, 1404—1410).

**Physical Properties of Mannitol and its Aqueous Solutions.** JOSEPH M. BRAHAM (*J. Amer. Chem. Soc.*, 1919, 41, 1707—1718).—The melting point, the specific rotation in aqueous solution, and the freezing-point solubility diagram of pure mannitol up to  $103^\circ$  have been determined. The most trustworthy values of the density, specific heat, and heat of combustion are indicated from a discussion of the various values occurring in the literature. The following physical constants are recorded: melting point,  $166.05^\circ$ ; specific rotation,  $[\alpha]_D^{25} = -0.244 \pm 0.002^\circ$ , and  $[\alpha]_D^{25}$  calculated =  $-0.208 \pm 0.002^\circ$ ;  $D$  1.487 (room temperature), specific heat  $C$  ( $28\text{--}100^\circ$ ) =  $0.3271$  cal./deg., and  $C$  ( $14\text{--}26^\circ$ ) =  $0.315$  cal./deg.;

heat of combustion, 4.00 cal./gram. Pure mannitol may be obtained from the commercial product by two crystallisations from aqueous alcohol. J. F. S.

**Conversion of the Simple Sugars into their Enolic and Ethylene Oxide Forms.** EDWARD FRANKLAND ARMSTRONG and THOMAS PERCY HILDITCH (T., 1919, 115, 1410—1428).

**Action of the Carbonates of the Alkaline Earths on Dextrose.** HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1919, 97, 97—113).—When a solution of dextrose is boiled with calcium carbonate, it becomes brown, and gradually loses its dextro-rotation, which after prolonged boiling is entirely eliminated; the sugar may even become lævorotatory. The reducing power of the dextrose is also diminished, but to a much smaller extent. Distilled water previously shaken with calcium carbonate produces the same change, but the reduction in the rotation becomes constant after some time because the dissolved carbonate is neutralised by the acid formed in the reaction. It is concluded that the dextrose is changed into lævulose, and eventually into other lævorotatory or weakly dextro-rotatory sugars. S. S. Z.

**Synthesis of Disaccharides with Two Sulphur or Selenium Atoms.** FRITZ WREDE (*Ber.*, 1919, 52, [B], 1756—1761).—Acetobromoglucose reacts with potassium disulphide in alcohol to form a disulphide of the type  $R_2S_2$ , mixed with various by-products. Some of these are partly de-acetylated compounds, but they may be re-acetylated by means of acetic anhydride and the complication thus removed. To a certain extent the potassium disulphide reacts as a mixture of sulphur and monosulphide, the latter forming the octa-acetate of thioisotrehalose,  $R_2S$  (A., 1917, i, 540), and apparently also according to the scheme  $R_2S_2 + 2K_2S = 2R \cdot SK + K_2S_2$ . The mono- and di-sulphides can be separated by fractional crystallisation, and the acetyl groups removed by means of methyl-alcoholic ammonia. Similar selenium compounds may also be obtained.

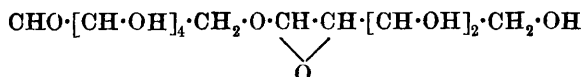
*Octa-acetyldithiodiglucose*,  $C_{28}H_{38}O_{18}S_2$ , crystallises in stout crusts from benzene or long needles from methyl alcohol; m. p.  $139^\circ$ ,  $[\alpha]_D^{18} - 177.7^\circ$  in nitrobenzene. *Dithiodiglucose*,  $C_{12}H_{22}O_{10}S_2$ , is a hygroscopic, white powder,  $[\alpha]_D^{18} - 144.4^\circ$  in water, which tastes sweet, and forms metallic salts, for example, the *potassium salt*,  $C_{12}H_{20}O_{10}S_2K_2 \cdot 2H_2O$ . *Octa-acetyldiselenodiglucose* has m. p.  $133^\circ$ ,  $[\alpha]_D^{18} - 133.8^\circ$  in chloroform, and *diselenodiglucose* is a pale yellow powder,  $[\alpha]_D^{18} - 93.98^\circ$  in water, which forms a *potassium salt*,  $C_{12}H_{20}O_{10}Se_2K_2 \cdot 2H_2O$ . J. C. W.

**Density of Pure Sucrose and the Contraction in Volume of its Aqueous Solutions.** D. SIDERSKY (*Bull. Assoc. Chim. Sucr. Dist.*, 1919, 37, 73—77).—From the tables of specific gravities of aqueous sucrose solutions compiled by Plato in 1900 (and adopted by the German *Normal Eichungs-Kommission*), the author has calculated the solution density of sugar at different concentrations, the solvent being assumed to occupy the same volume as in the pure

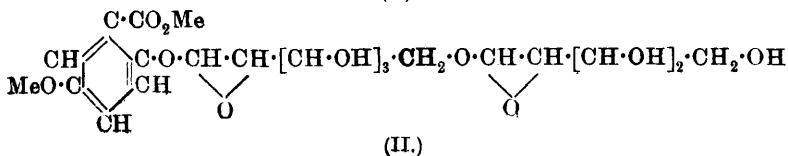
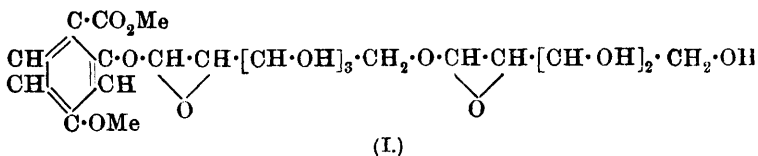
state. For concentrations ranging from 5 to 90 grams of sucrose per 100 c.c. absolute, at 15°, the solution densities range almost linearly from 1·629 to 1·591, thus approaching the density of solid sugar (1·588) as the limit of solubility is reached. The contraction which accompanies the formation of sucrose solutions increases with the concentration of sugar to a maximum value of 0·47% of the total volume for solutions containing 45—55 grams per 100 c.c., beyond which concentration it declines again, and amounts to only 0·11% for solutions containing 90 grams per 100 c.c. J. H. L.

**Characteristics and Composition of Primeverose.** A. GORIS and CH. VISCHNIAC (*Compt. rend.*, 1919, 169, 871—873).—A further study of the sugar primeverose, obtained from the two glucosides primeverin and primulaverin isolated from *Primula officinalis*, Jacq (compare A., 1913, i, 576). This sugar crystallises in the anhydrous state and has m. p. 209—210°. It shows mutarotation, initial  $[\alpha]_D + 22·70^\circ$ , final  $[\alpha]_D - 3·43^\circ$ . It reduces Fehling's solution, gives an *osazone*, m. p. 224—225°, and on hydrolysis gives one molecule of dextrose and one molecule of xylose. W. G.

**Constitution of Primeverose, Primeverin, and Primulaverin.** A. GORIS and CH. VISCHNIAC (*Compt. rend.*, 1919, 169, 975—977).—It has previously been shown (preceding abstract) that primeverose is a biose formed by the combination of a molecule of dextrose and a molecule of xylose, and that it has a free aldehyde group. It has now been shown by controlled oxidation of the sugar and subsequent hydrolysis of the *calcium primeverobionate* formed that the free aldehyde group is in the dextrose residue. The constitution of primeverose is, therefore, given as



Similarly, it has been shown that primeverin and primulaverin give, on hydrolysis, primeverose and the methyl esters of  $\beta$ -methoxyresorcylic acid and *m*-methoxysalicylic acid respectively. These two compounds have, therefore, the constitutions shown in formulæ I and II respectively:



W. G.

**Systematic Ageing Experiments with Solutions of Various Kinds of Starch under Exact Time Conditions. Time Law of the Ageing of Starch Solutions.** HERMANN SALLINGER (*Kolloid Zeitsch.*, 1919, 25, 111—115).—Experiments on the ageing of starch solutions have been carried out with soluble potato starch, soluble wheat starch, soluble barley starch, and with amyloextrin from potato starch. The solutions were made up in water, and at stated intervals 50 c.c. of the solution were treated with 0.5 c.c. of human saliva (ptyalin) and kept for twenty-three hours at the ordinary temperature; the precipitated starch gel was filtered and dried at  $110^{\circ}$  until of constant weight. If  $G$  is the weight of gel and  $t$  the time of ageing in hours it is found that the relationship between  $\log G$  and  $\log t$  is represented by a straight line, and that numerically  $G = gt^a$ , where  $g$  and  $a$  are constants. These values have been determined for the starch varieties named above, and it is shown that they are characteristic of the variety. The following values are recorded: potato starch I.,  $g = 4.06$ ,  $a = 0.445$ ; potato starch II.,  $g = 3.00$ ,  $a = 0.455$ ; wheat starch,  $g = 5.37$ ,  $a = 0.165$ ; barley starch,  $g = 11.17$ ,  $a = 0.214$ ; amyloextrin,  $g = 3.51$ ,  $a = 0.521$ . The starch solutions were aged at  $7^{\circ}$ . J. F. S.

**Studies in Fermentation.** HERMANN SALLINGER (*Fermentforsch.*, 2, 449—457; from *Chem. Zentr.*, 1919, iii, 635).—A reply to Biedermann (A., 1917, i, 62). The author sets out in detail the reasons which lead him to consider the application of extremely dilute solutions, as recommended by Biedermann, unsuitable. Experiments with sterilised starch solution failed to confirm the diastatic action of saliva ash or the autolysis of starch. H. W.

**Studies in Fermentation. IV. Autolysis of Starch.** W. BIEDERMANN (*Fermentforsch.*, 2, 458—472; from *Chem. Zentr.*, 1919, iii, 635).—The autolysis of starch might possibly be due to traces of ferments retained by the crude material. The former experiments (A., 1917, i, 62; 1919, i, 107) have therefore been repeated with preparations of amylose which had been purified by boiling and treatment with hydrochloric acid. The experimental procedure is very fully described. The author has endeavoured to disprove the possible criticism that the results are due to bacterial action by control experiments in which a culture of bacteria which readily cause the fission of starch was added to the amylose solution; the achromic point was reached very much more slowly than in the presence of saliva ash or sodium chloride. The activity of the salts is not due to their power of directly causing the fission of starch, but is to be ascribed to their action in facilitating the formation of the ferment; when once this is attained in a sufficient degree, autolysis proceeds unaltered in a solution which has been freed from salts by dialysis. Preparations which already contain fission products of starch are less readily affected, and require much longer periods than pure amylose preparations. H. W.

**Cellulose and Cellulose Nitrate. Absorbent Power for Gases and Constitution.** B. Oddo (*Gazzetta*, 1919, 49, ii, 127—139).—Cellulose is able to fix acid gases in definite proportion, one molecule of dry hydrogen chloride being taken up per one quadrupled molecule ( $C_{24}$ ) of cellulose. Of the other gases examined only ammonia is absorbed in approximately the above proportion. In all cases the volumes of different gases absorbed increase with their solubility in water and diminish in the following order:  $NH_3$ ,  $HCl$ ,  $SO_2$ ,  $H_2S$ ,  $N_2O$ ,  $CO_2$ ,  $C_2H_2$ ,  $CO$ ,  $O$ ,  $N$ ,  $CH_4$ ,  $H$ . Charcoal which has absorbed a certain gas loses part of this when immersed in a second gas, the latter being absorbed to some extent without chemical action taking place. A similar phenomenon sometimes occurs with cellulose, but whereas carbon dioxide displaces ammonia and sulphur dioxide, it does not displace hydrogen chloride. The latter appears, therefore, to enter into true chemical combination, either being added to the ethereal oxygen with formation of an oxonium compound,  $:O\text{<} \begin{smallmatrix} H \\ Cl \end{smallmatrix}$ , or giving a grouping similar to that obtained with aldehydic compounds,  $\cdot CH:O + HCl = \cdot CHCl \cdot OH$ .

By deca- and endeca-nitrated celluloses dry hydrogen chloride is at first absorbed with great rapidity, but after a time red vapours are emitted and, even after being kept in an evacuated space, the product contains ionic chlorine and small proportions of nitrogen. The volume of sulphur dioxide absorbed by nitrated cellulose (13.32% N) is about five times that absorbed by an equal weight of cellulose.

T. H. P.

**Nitroacetylcellulose [Cellulose Nitrate Acetate].** B. Oddo (*Gazzetta*, 1919, 49, ii, 140—145).—The author has prepared a cellulose nitrate acetate by the action of boiling acetic anhydride on a collodion cotton (11.68% N), probably consisting principally of octanitrated cellulose,  $C_{24}H_{28}O_8(O \cdot NO_2)_8(OH)_4$ . The percentage of nitrogen and the number of acetyl groups in the product obtained indicate it to be a tetra-acetate octanitrate of cellulose, but cryoscopic determination of the molecular weight in acetic acid at low concentrations (0.42—2.1%) gives results corresponding closely with the formula  $C_6H_7O_2(O \cdot NO_2)_2 \cdot OAc$ ; as the concentration of the solution is increased, the molecular weight also increases, and reaches the quadruple value only when the concentration is about 21%. When purified, the substance is quite white, and begins to contract at  $175^\circ$ , whilst at  $184.5^\circ$  it decomposes with evolution of gas bubbles. It does not reduce Fehling's solution, but, like cellulose nitrate, gives a yellow coloration when moistened with dilute sulphuric acid and treated with a solution of iodine in potassium iodide. In the air it burns rapidly with an orange-yellow flame, leaving a small, partly carbonised residue. It dissolves in the hot in dilute, and in the cold in concentrated, alkali hydroxide solution; it is soluble in concentrated sulphuric acid, addition of mercury to the solution resulting in the liberation of nitric oxide.

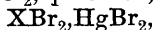
T. H. P.

**The Use of Thallium in Organic Chemistry.** KARL FREUDENBERG and GERTRUD UTHEMANN (*Ber.*, 1919, **52**, [B], 1509—1513).—Thallium hydroxide or carbonate has proved useful in the isolation of acids of the gallic acid series (A., 1919, i, 413), and it is now shown that uric acid, phthalimide, and lævulose give well-defined *thallium* salts. Glycine may also be prepared from the hydrochloride of its ester by boiling this with thallium carbonate and water, filtering the precipitate of thallium chloride, saturating with hydrogen sulphide, and filtering again.

Solutions of convenient thallium compounds are prepared as follows. Thallium turnings are suspended over alcohol in an atmosphere of oxygen, when oily thallium "ethoxide" is produced, and also a 5% solution of this in alcohol. The oil is really a mixture or compound of ethoxide and hydroxide in slightly varying proportions, formed according to the equation  $2\text{Tl} + \text{O} + \text{EtOH} = \text{TlOEt} + \text{TlOH}$ . It is freely soluble in pure ether. The hydroxide is obtained by mixing the oil with water and evaporating the alcohol under reduced pressure. The saturated aqueous solutions are about 2*N* (400 grams per litre). A concentrated solution of a hydrogen carbonate (200 grams Tl per litre) is produced by saturating a suspension of the hydroxide with carbon dioxide.

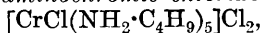
J. C. W.

**Alkylamino-chromium Compounds. IV. Compounds with Methyl-, *n*-Butyl-, and *iso*-Amyl-amines.** HJ. MANDAL (*Ber.*, 1919, **52**, [B], 1489—1500. Compare A., 1919, i, 257).—The following *chloropentamethylaminochromic* salts have been prepared: chloride,  $[\text{CrCl}(\text{NH}_2\text{Me})_5]\text{Cl}_2$ , by the action of methylamine on anhydrous chromic chloride at  $-10^\circ$  (Lang and Carson, A., 1904, i, 800); *bromide*, glistening, violet prisms, and *iodide*, by double decomposition of the chloride with the potassium haloid; *mercurichloride*,  $\text{XCl}_2 \cdot 3\text{HgCl}_2$ , pale red, *mercuribromide*,

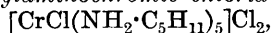


reddish-violet, stellate groups, and red *mercuri-iodide*,  $\text{XI}_2 \cdot \text{HgI}_2$ , by the addition of the potassium mercuri-haloids to the above haloids; *platinichloride*,  $\text{XPtCl}_6$ , microcrystalline, chamois-coloured powder, and *bismuthichloride*,  $\text{XCl}_2 \cdot \text{BiCl}_3$ , pale violet, by the addition of the metallic chloride to hydrochloric acid solutions of the above chloride; yellow *pentasulphide*,  $\text{XS}_5$ , by the addition of yellow ammonium sulphide to the chloride.

*Chloropenta-*n*-butylaminochromic chloride*,

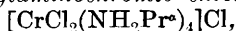


and *chloropentaisoamylaminochromic chloride*,



are obtained by gently boiling the amines with chromic chloride. They are successively deeper violet in colour than the lower isomerides, but they are decomposed by water and are not easy to purify.

*Dichlorotetra-*n*-propylaminochromic chloride*,



is formed as a by-product in the preparation of the pentapropylamine compound (*loc. cit.*) if the mixture becomes too hot. It crystallises in very dark green prisms, and the *nitrate* is greyish-green. *Dichlorotetra-n-butylaminochromic chloride*, small, green prisms, and *dichlorotetraisoamylaminochromic chloride*, a greyish-green powder, are prepared by the addition of concentrated hydrochloric acid to alcoholic solutions of the penta-alkylamino-compounds.

J. C. W.

**Manufacture of Salts or Compounds of Choline and of its Higher Homologues.** VEREINIGTE CHEMISCHE WERKE (Brit. Pat., 8031 of 1914).—Solutions of the compounds or salts of choline with such acids as boric, salicylic, *o*-, *m*-, or *p*-iodobenzoic, *p*-aminophenylarsinic, 3-iodo-4-aminophenylarsinic, or formic acid, whilst having a similar action to choline itself on cell tissues when injected into the blood, have the advantage of increased stability and consequent non-formation of poisonous decomposition products. The action of these compounds is therefore quite different from that of salts of choline with mineral acids, which have a negligibly small action on living cells. [See, further, *J. Soc. Chem. Ind.*, 1920, 43A.]

G. F. M.

**The Decomposition of Carbamide in the Presence of Nitric Acid.** TUDOR WILLIAMS PRICE (T., 1919, 115, 1354—1360).

**Compounds of Complex Cyanides with Mercuric Cyanide.**

D. STRÖMHOLM (*Zeitsch. anorg. Chem.*, 1919, 108, 111—112).—When a warm, concentrated aqueous solution of equivalent quantities of potassium platinocyanide and mercuric cyanide is allowed to cool, white, crystalline needles of a double salt having the composition  $K_2Pt(CN)_4.Hg(CN)_2.2H_2O$  separate. A similar compound of potassium nickel cyanide and mercuric cyanide was prepared. Mercuric cyanide does not form compounds with potassium ferricyanide, cobalticyanide, chromicyanide, or with the compound  $K_4Mo(CN)_8$ .

E. H. R.

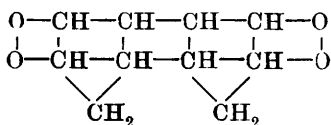
**The Constitution of the Nitroprussides. I. Conductivity and Cryoscopic Measurements.** GEORGE JOSEPH BURROWS and EUSTACE EBENEZER TURNER (T., 1919, 115, 1429—1435).

**Action of Acetylene on Arsenic Trichloride.** ORVILLE A. DAFERT (*Monatsh.*, 1919, 40, 313—323).—Acetylene does not react to any considerable extent with arsenic chloride at the ordinary temperature or at the boiling point of the latter; in the presence of anhydrous aluminium chloride at the ordinary temperature, however, *diacetylene arsenic trichloride*,  $AsCl_3.2C_2H_2$ , is readily formed as a heavy, yellow oil,  $D^{15}$  1.6910, b. p. 250°. Its vapours are strongly irritating, but not markedly poisonous, although exhibiting strong bactericidal power. When compared with the corresponding antimony and aluminium compounds, the arsenic

derivative exhibits a remarkable stability, since it can be distilled and is not decomposed by water. When heated with potassium hydroxide solution, it evolves acetylene. At a higher temperature, arsenic trichloride and acetylene in the presence of aluminium chloride yield a black, organo-arsenic compound of high molecular weight which is very stable towards reagents, but sensitive to light, and in its properties resembles the aluminium derivative prepared by Baud in a similar manner; it contains 7.70% As, 69.25% C, 5.18% H, and 7.87% O. [Total, 90% only.] H. W.

**Organo-metallic Compounds. II. The Action of Carbon Monoxide on Sodium Alkyls.** HANS HEINRICH SCHLUBACH (*Ber.*, 1919, **52**, [B], 1910—1914).—Carbon monoxide is readily absorbed by mixtures of sodium and mercury diethyl or mercury diphenyl in light petroleum or benzene, that is, by the organo-sodium compounds (compare Schlenk, A., 1917, i, 255). In the case of sodium ethyl the products are diethyl ketone, triethylcarbinol, and propionic acid, whilst the smoother reaction in the case of sodium phenyl gives rise to benzophenone (30%), triphenylcarbinol (25%), and benzoic acid (16%), the yields being calculated on the weight of mercury diphenyl used. J. C. W.

**cyclopentadiene and its Dimeride.** HANS STOBBE and FRITZ DÜNNHAUPT (*Ber.*, 1919, **52**, [B], 1436—1442).—From the result of refraction measurements made a few years ago, Stobbe concluded that cyclopentadiene changes almost completely into a dimeride within thirty days at 20° (A., 1912, i, 842). The nature of the atmosphere above the oil, whether air or carbon dioxide, seemed to have no great influence on the rate at which the refractive index rose. Inasmuch as the hydrocarbon, and especially its dimeride, spontaneously absorb oxygen, it remained to be proved whether the polymerisation is accompanied by autoxidation. It is actually found that the end-product of the polymerisation when the oil is freely exposed to oxygen is not the dimeride, but its di-peroxide, probably represented by the annexed formula. In the absence of oxygen, the end-product has a slightly greater refractive index. The rate at which polymerisation proceeds is distinctly, but only very slightly, greater in the light than in the dark. J. C. W.



**The Benzene [Formula] Problem. II.** A. VON WEINBERG (*Ber.*, 1919, **52**, [B], 1501—1508).—See this vol., ii, 14.

**Catalytic Oxidation of Benzene.** JOHN M. WEISS and CHARLES R. DOWNS (U.S. Pat. 1318633).—Benzene is oxidised to compounds containing hydrogen, oxygen, and less than six carbon atoms by the action of a gas containing oxygen at a temperature of 300—500° in the presence of a catalyst. G. F. M.



**Oxidation of Side-chains with Potassium Permanganate.**

LUCIUS A. BIGELOW (*J. Amer. Chem. Soc.*, 1919, **41**, 1559—1581).

—The action of potassium permanganate in alkaline solution on three nitrotoluenes has been investigated. The experiments were generally performed by gradually adding the solid permanganate to a boiling suspension of the nitrotoluene in aqueous sodium hydroxide solution; in the case of *p*-nitrotoluene, oxidation was also effected at lower temperatures, but the yields were considerably decreased and the duration of the experiments greatly prolonged.

Changes in the conditions of oxidation, in general, merely cause a different proportion of the nitrotoluene to be attacked by the oxidising action, the ratio of nitrobenzoic acid produced to unchanged nitrotoluene remaining essentially constant. The conclusions are therefore drawn that the quantity of nitrotoluene or nitrobenzoic acid entirely destroyed by the oxidising agent is practically constant and almost independent of the oxidation procedure, and that at least two entirely independent actions take place simultaneously in the oxidising mixture, namely, the oxidation of the organic compound and the decomposition of the permanganate into manganese oxides and free oxygen. It is somewhat curious to note, however, that solutions containing alkali and permanganate, in the proportions most frequently used in this work, do not decrease in oxidising power when boiled for protracted periods in the absence of organic matter.

Increase in the concentration of the alkali in the oxidising mixture up to a certain point favours the oxidation of *o*-nitrotoluene, beyond which point a further increase produces essentially no effect, all other conditions being kept constant. By this increase in alkaline concentration, the oxidation of the meta-isomeride is hindered, such oxidation being most effective in an essentially neutral medium; with *p*-nitrotoluene, oxidation is favoured up to a certain point, beyond which the quality of the product becomes very poor. Possibly, acceleration of the oxidation of the ortho- and para-isomerides by alkali is due to their conversion into a quinonoid form, which is impossible with the meta-derivative.

Increasing dilution of the reaction mixture favours the oxidation of all the nitrotoluenes, probably owing to retardation of the decomposition of the permanganate into manganese oxides and oxygen.

In all circumstances, *p*-nitrotoluene is oxidised most readily, the ortho-compound next, and the meta-isomeride least readily.

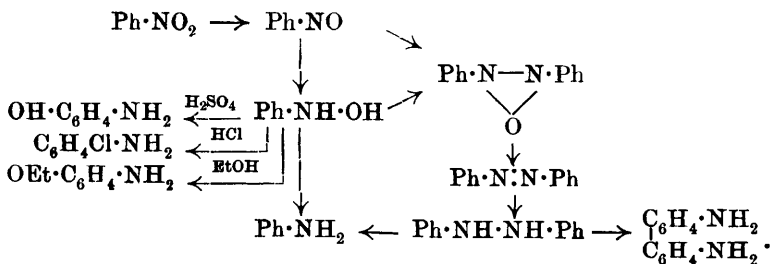
Catalytic influences have been studied by carrying out the oxidations of *o*- and *p*-nitrotoluenes in iron, copper, and enamel-lined vessels respectively. In both cases nearly the same results were obtained in the copper and enamel-lined containers, but distinctly lower yields and products of poorer quality in the iron vessel both with and without alkali. The addition of salts of calcium and magnesium to the reaction mixture in the oxidation of *p*-nitrotoluene in neutral solution produced no noticeable effect, and a similar result was obtained after addition of pyridine to a similar oxidation in alkaline solution, although it acts as a powerful negative catalyst in certain permanganate reactions.

A practical method for the preparation of *m*-nitrotoluene has been elaborated, consisting in the nitration of aceto-*p*-toluidide to *m*-nitroaceto-*p*-toluidide, hydrolysis of the acetyl group, and elimination of the amino-group; the details are fully discussed in the original paper. H. W.

**Production of Benzyl Chloride and Benzylidene Chloride and of certain Homologues and Substitution Products of these Compounds.** LEVINSTEIN, LTD., HERBERT LEVINSTEIN, and WALTER BADER (Brit. Pat. 134250).—Substitution products containing chlorine in the side-chain are obtained by treating hydrocarbons at temperatures below 0° with hypochlorous acid in aqueous solution. For example, toluene (3 mols.) is emulsified with a hypochlorite solution containing 1 mol. of active chlorine, and after cooling to -5° dilute sulphuric or other acid (1 equivalent) is gradually added. The product, containing unchanged toluene, 60—70% of the theoretical quantity of benzyl chloride, and small quantities of benzylidene chloride and higher chlorinated products, is purified by fractional distillation. A second atom of chlorine may be similarly introduced, it occupying preferably a position in the methyl group already substituted if more than one are present. Monochlorotoluenes behave similarly, but the higher chlorinated toluenes, nitro-substitution products, sulphonyl chlorides, and cresol esters do not give side-chain substitution products under these conditions. Sulphonic acids are substituted in the nucleus.

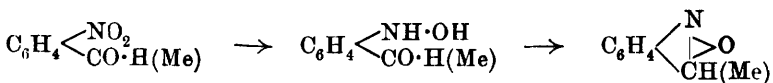
G. F. M.

**Determination of the Course of the Reaction in the Catalytic Reduction of Nitrobenzene.** F. F. NORD (Ber., 1919, 52, [B], 1705—1712).—In the reduction of nitrobenzene by chemical or electrical means, it is evident that phenylhydroxylamine plays an important part, as the following scheme indicates:



It appeared to be of interest, therefore, to determine whether it is formed during the catalytic reduction of nitrobenzene by means of colloidal platinum protected by gum arabic, but this mode of reduction offers very little scope for controlling the rate of the reaction and isolating any intermediate products, compared with the electrolytic method. To surmount this difficulty, the reduction of *o*-nitrobenzaldehyde and *o*-nitroacetophenone was tested, for the aldehyde or ketone group in the ortho-position is capable of form-

ing anthranils through condensation with the hydroxylamine group, thus:



(compare Bamberger and others, A., 1904, i, 93; 1909, i, 509, 511). By stopping the reaction after two molecular proportions of hydrogen were absorbed, the anthranils could, indeed, be isolated.

The rate at which nitrobenzene is reduced to aniline is practically constant, and so it is during the reduction of *o*-nitroacetophenone to *o*-aminoacetophenone, the yields being quantitative. In the case of *o*-nitrobenzaldehyde, however, there is a very considerable lag after the anthranil stage is reached. The absorption of the third molecular proportion of hydrogen takes about twelve times as long and the product contains only a small quantity of *o*-aminobenzaldehyde. The chief product is Friedländer and Göhring's pale yellow condensation product of *o*-aminobenzaldehyde, m. p. 183—186° (A., 1884, 1019).  
J. C. W.

**The Nitrotoluenes. I. Binary Systems of a Nitrotoluene and *s*-Trinitro-*m*-xylene.** JAMES M. BELL and JAMES P. SAWYER (*J. Ind. Eng. Chem.*, 1919, 11, 1025—1028).—Determinations have been made of the freezing points of binary systems in which one component was 2:4:6-trinitro-*m*-xylene and the other a nitrotoluene, and also of ternary systems containing two of these nitrotoluenes and 2:4:6-trinitro-*m*-xylene. The cooling-curve method was used for the determinations. In the case of mixtures of trinitro-*m*-xylene with the nitrotoluenes the eutectic temperatures (corr.) were as follows: with 2:4:6-trinitrotoluene, 74·8° (corresponding with 8% of the trinitroxylene); with 2:4-dinitrotoluene, 67·7° (corresponding with 6% of trinitroxylene); and with *p*-nitrotoluene, 50·5° (corresponding with 2%). The binary eutectic temperature for the mono- and dinitro-toluenes (26·4°) was lowered to 25·7° by the addition of trinitroxylene, and a similar lowering was observed on adding trinitroxylene to binary mixtures of the other nitrotoluenes. The relationship between the composition and m. p. of mixtures is shown by the equation  $\log_e x = -Q(T_0 - T)/RTT_0$ , where  $Q$  represents the molecular heat of fusion,  $T_0$  is the m. p. of the pure substance,  $T$  its m. p. in the presence of a second component, and  $x$  the molecular fraction of the melting component. The value of  $Q$  calculated from the points on the curve for trinitro-*m*-xylene and trinitrotoluene,  $x=0\cdot337$  and  $T=138\cdot1^\circ$  C. or  $411\cdot1^\circ$  A., was found to be 9200 cal. Substitution of these values in the above equation gave  $T=2012\cdot7/4\cdot424 \log_{10} x$ . This gave results agreeing well with the observed results in the case of mononitrotoluene, but in the case of the other two nitrotoluenes there was considerable deviation for the eutectic mixtures up to about 20% of trinitro-*m*-xylene.  
C. A. M.

**The Nitrotoluenes. II. Refractive Indices of Mixtures of *p*-Nitrotoluene, 2 : 4-Dinitrotoluene, and 2 : 4 : 6-Trinitrotoluene.** JAMES M. BELL and EDMUND O. CUMMINGS (*J. Ind. Eng. Chem.*, 1919, **11**, 1028—1029).—The refractive indices of mixtures of *p*-nitrotoluene, dinitrotoluene, and trinitrotoluene were determined at 38—39°, and the results expressed in relation to the composition of the mixtures in a triangular diagram showing the lines of equal refractive index. The results, which were confined to mixtures freezing below 40° (the eutectic temperatures being about 17°), agreed in all but a few instances (within the limits of experimental error) with the values calculated by means of the formula  $n = 1.542m + 1.572d + 1.580t$ , where *m*, *d*, and *t* represent the respective weights of mono-, di-, and tri-nitrotoluene in a mixture.

C. A. M.

**The Conductivities of Iodoanilinesulphonic Acids.** (MISS) MARY BOYLE (T., 1919, **115**, 1505—1517).

**Preparation of [Derivatives] of *p*-Toluenesulphonic Acid Halogenated in the Side-chain.** SOCIETY OF CHEMICAL INDUSTRY IN BASLE (D.R.-P. 312959; from *Chem. Zentr.*, 1919, iv, 373—374).—*p*-Toluenesulphonic acids or their dry salts are treated at an elevated temperature with halogens or substances which yield halogens, and in the presence or absence of halogen carriers. *ω*-Chloro- or di-*ω*-chloro- or *ω*-bromo- or di-*ω*-bromo-toluene-*p*-sulphonic acids are obtained according to the amount of halogen used and the experimental conditions employed. The sodium salts of *ω*-chlorotoluene-*p*-sulphonic acid and *ω*-*o*-dichlorotoluene-*p*-sulphonic acid are particularly described.

H. W.

**New Halogenated Sulphones.** A. PURGOTTI (*Ann. R. scuola superiore d'agr. in Portici*, 1915—1916, (2), **13**, 8 pp.).—The sulphones were obtained by the action of alkyl or aryl haloids on a boiling alcoholic solution of sodium *p*-chlorobenzenesulphinate for fourteen to twenty hours. Thus, methyl iodide yields *p*-chloro-phenylmethylsulphone, slender, needle-shaped, vitreous crystals, m. p. 57—58°, which is not reduced by nascent hydrogen or oxidised by permanganate. Ethyl bromide yields *p*-chlorophenylethylsulphone, white crystals, m. p. 260—261° (decomp. at a slightly higher temperature), which is very stable to oxidising and reducing agents. *iso*Propyl bromide yields *p*-chlorophenylisopropylsulphone, vitreous prisms, m. p. 226—227°, which is unaltered by oxidising or reducing agents. Ethylene dibromide yields di-*p*-chlorophenylethylenedisulphone, silky laminæ, m. p. 237—238°, which is not attacked by oxidising agents, but is converted into 2 mols. of *p*-chlorophenyl methyl sulphone by zinc and hydrochloric acid. *p*-Chlorophenylbenzylsulphone, prepared from benzyl chloride, forms white laminæ, and has m. p. 257—258°; oxidising agents change it into benzoic acid and *p*-chlorobenzenesulphonic acid. *p*-Chlorophenyl-2 : 4 : 6-trinitrophenylsulphone, pre-

pared from picryl chloride, forms a dense, brownish-red oil, which, after twenty-four hours, solidifies to a crystalline mass; after recrystallisation, this forms yellow, lustrous needles, m. p. 104—105°. If heated slowly it decomposes at about 200°, but if heated quickly explodes violently.

CHEMICAL ABSTRACTS.

**A Method for the Preparation of Aromatic Selenonic Acids. *o*- and *p*-Xyleneselenonic Acids.** RICHARD ANSCHÜTZ JOSEF KALLEN, and KARL RIEPENKRÖGER (*Ber.*, 1919, **52**, [B], 1860—1875).—The xylenes react with 96% selenic acid (the preparation of which is described) in the presence of acetic anhydride at 0°, giving white crystals of the very hygroscopic selenonic acid. The position of the substituent has not been determined, but it is probable that one compound is *p*-xylene-2-selenonic acid, m. p. 95—96°, and the other *o*-xylene-4-selenonic acid, m. p. 108—110°. Salts of ten metals are described, as well as the corresponding salts of the sulphonic acids, most of which are new. Most attention is paid to the molecules of water of crystallisation, the numbers of which are set out in the following table:

Acid.	NH <sub>4</sub> .	K.	Na.	Ba.	Mg.	Zn.	Ag.	Cu.	Ni.	Co.
<i>p</i> -Xyleneselenonic.....	0	0	4	3	8	10	1	10	7	9
„ sulphonic ...	0	1	1	0	8	10	1	5	7	9
<i>o</i> -Xyleneselenonic ...	0	0	4	3	0	6	0	6	5	5
„ sulphonic ...	0	0	5	2	5	5	0	6	6	5

J. C. W.

**$\omega\omega'$ -Diarylparaffins and  $\omega$ -Arylparaffincarboxylic Acids.** W. BORSCHÉ (*Ber.*, 1919, **52**, [B], 2077—2085).—The author has applied Clemmensen's method of reduction to a number of mono- and di-ketones which had previously served as starting point in the preparation of  $\omega\omega'$ -diarylparaffins (Borsche and Wollemann, *A.*, 1913, i, 171). In general, it is found that  $\alpha\beta$ -unsaturated ketones yield only small quantities of the corresponding saturated hydrocarbons when reduced by amalgamated zinc and concentrated hydrochloric acid, large amounts of resin being formed. The corresponding saturated mono- and the saturated di-ketones, on the other hand, give satisfactory yields of the hydrocarbons. The method may also be successfully employed in the reduction of a number of ketonic acids.

$\alpha\epsilon$ -Dianisylpentane, a colourless, oily liquid, b. p. 264—266°/30 mm., is prepared by the reduction of  $\alpha\epsilon$ -di-*p*-methoxyphenylpentane- $\gamma$ -one by zinc and hydrochloric acid; the corresponding phenol, b. p. 300—301°/32 mm., is obtained by the reduction of  $\alpha\epsilon$ -di-*p*-hydroxyphenylpentane- $\gamma$ -one, colourless oil, b. p. 313—314°/14 mm., and yields a tetranitro-derivative, pale yellow crystals, m. p. 146—148° (decomp.).  $\alpha\zeta$ -Di-*m*-4-xylylhexane forms colourless leaflets, m. p. 76—77°, b. p. 247—248°/20 mm. (formed from  $\alpha\zeta$ -di-*m*-4-xylylhexane- $\alpha\zeta$ -dione, colourless needles, m. p. 125—126°, which results, together with *m*-4-xyloylvaleric acid, colourless needles, m. p. 98—99°, from the condensation of adipyl chloride

with *m*-xylene in the presence of aluminium chloride [compare Veckenstedt, *Inaug. Diss.*, Göttingen, 1911]. *aθ-Di-m-4-xyl-yloctane*, colourless needles, m. p. 63—64°, b. p. 253—254°/13 mm., is obtained from *aθ-di-m-4-xyl-yloctane-aθ-dione*, yellow needles, m. p. 78—79°. Reduction of *a-di-p-tolyl-nonane-a-dione*, slender, colourless needles, m. p. 78—79°, leads to the formation of *a-di-p-tolyl-nonane*, m. p. 48—49°, b. p. 248—252°/18 mm. (*ω-p-toluoyloctoic acid* has m. p. 98°). *ακ-Di-m-4-xyl-yldecane-ακ-dione*, slender, intertwined needles, m. p. 61°, could not be reduced to the corresponding hydrocarbon by Clemmensen's or Paal's process.

The following acids have been prepared by Clemmensen's method from the ketonic acids or their esters: *γ-p-tolyl-n-butyric acid*, colourless leaflets, m. p. 58—59°, from *β-p-toluoylpropionic acid*; *γ-β-naphthyl-n-butyric acid*, colourless leaflets, m. p. 100° (*ethyl ester*, colourless oil, b. p. 216—218°/20 mm.); *ε-phenylhexoic acid*, b. p. 206—208°/30 mm.; *η-phenyloctoic acid*, colourless leaflets, b. p. 209—210°/14 mm.; *ι-phenyldecoic acid*, m. p. 41°, b. p. 228—230°/18 mm. (*ethyl ester*, b. p. 220—224°/20 mm.). It should be noted that in the reduction of the acids with amalgamated zinc and hydrochloric acid in the presence of a relatively small amount of alcohol, esterification of the organic acid frequently occurs to some extent.

The following products have been obtained from adipyl chloride and toluene, *p*-xylene, and mesitylene respectively: *αζ-di-p-tolyl-hexane-αζ-dione*, m. p. 144—145°, and *δ-p-toluoylvaleric acid*, m. p. 153—154°; *αζ-di-p-3-xyl-ylohexane-αζ-dione*, m. p. 127—128°, and *δ-p-3-xyl-ylovaleric acid*, m. p. 132—133°; *αζ-dimesitylhexane-αζ-dione*, m. p. 102—103°, and *δ-mesitylvaleric acid*, crystalline mass, b. p. 236°/13 mm. Glutaryl chloride and *m*-xylene yield *αε-di-m-4-xyl-ylpentane-αε-dione*, m. p. 60—61°, and *γ-m-xyl-ylobutyric acid*, m. p. 118°.

H. W.

**Preparation of Nitro-compounds of Tetrahydronaphthalene and its Homologues.** TETRALIN G.M.B.H. (D.R.-P. 299014; from *Chem. Zentr.*, 1919, iv, 374).—Tetrahydronaphthalene, or its homologues, is treated with nitric-sulphuric acid or other nitrating mixtures which do not contain more than 25% of water in such a manner that the temperature does not exceed 50° in the first phases of the action. In these circumstances, oxidation and resinification are almost completely avoided. Tetrahydronaphthalene and nitric-sulphuric acids give a mixture of *α*- and *β*-nitrotetrahydronaphthalene, b. p. 121—128°/0.17 mm., which is also obtained when concentrated nitric acid (D 1.47) is gradually added to a solution of tetrahydronaphthalene in acetic anhydride, a mixture of acetic acid and acetic anhydride, or an indifferent solvent. A mixture of nitric acid (D 1.47, 160 parts) and sulphuric acid monohydrate (200 parts) yields 1:3-dinitrotetrahydronaphthalene, yellow crystals, m. p. 71—72°, which is oxidised to 3:5-dinitrophthalic acid, m. p. 226°, by moderately concentrated nitric acid. It decomposes when heated, and forms an explosive

mixture with potassium chlorate, ammonium nitrate, etc. It is converted by a mixture of fuming sulphuric and nitric acids into *trinitrotetrahydronaphthalene*, yellowish-white crystals, m. p. 80—81°. H. W.

### Triphenylmethyl. XXIX. Diphenyl- $\alpha$ -naphthylmethyl.

M. GOMBERG and C. S. SCHOEFFLE (*J. Amer. Chem. Soc.*, 1919, **41**, 1655—1676. Compare A., 1918, i, 111).—The investigation was undertaken with the object of preparing a compound possessing a considerably greater degree of dissociation than triphenylmethyl to determine whether this attribute would be accompanied by an enhancement of the various chemical characteristics of the latter, and to determine with a high degree of accuracy the molecular weight of the free radicle in various solvents covering a wide range of temperature in order to ascertain the influence of temperature on the molecular state of the free radicle.

*Diphenyl- $\alpha$ -naphthylmethyl chloride*, large, colourless crystals, m. p. 170—171°, is most conveniently prepared by the action of the calculated quantity of acetyl chloride on diphenylnaphthylcarbinol dissolved in benzene; the corresponding *bromide* has m. p. 165—166° (slight decomp.), whilst *diphenylnaphthyl ethyl ether* forms well-defined, colourless crystals, m. p. 132°. *Diphenyl- $\alpha$ -naphthylmethyl* is obtained by the action of molecular silver on a solution of the chloride in benzene, and forms practically colourless crystals, which gradually become pale yellow, m. p. about 135—137° after darkening at 130°. The radicle absorbs oxygen very rapidly, but in spite of the fact that the theoretical amount of the gas is absorbed, diphenylnaphthylmethyl, like triphenylmethyl, does not give the theoretical quantity of peroxide. It readily reacts with iodine, and an equilibrium is attained,  $\text{CPh}_2\cdot\text{C}_{10}\text{H}_7 + \text{I} \rightleftharpoons \text{CPh}_2\text{I}\cdot\text{C}_{10}\text{H}_7$ , when approximately 60% of the radicle has been changed; attempts to isolate the iodide were unsuccessful, but its formation is definitely established by the isolation of the corresponding *anilide*, m. p. 151°. When an excess of iodine is added to the solution of diphenylnaphthylmethyl, an unstable periodide separates as an oil. When treated with hydrogen chloride in benzene solution, the free radicle is converted to the extent of more than 80% into diphenylnaphthylmethane and diphenylnaphthylmethyl chloride, the remainder being transformed into a *polymeride*  $\text{C}_{46}\text{H}_{34}$ , very fine, colourless crystals, m. p. 234—235°, the molecular weight of which appears to be abnormal. Reduction by hydrogen in the presence of platinum black converts diphenylnaphthylmethyl into diphenylnaphthylmethane.

Attempts are described to prepare additive compounds of the free radicle with ethyl and ethyl amyl ethers, amyl formate, ethyl acetate, amyl acetate, ethyl chloroacetate, ethyl valerate, acetone, dipropyl ketone, methyl butyl ketone, acetonitrile, propionitrile, benzene, toluene, xylene, and hexane respectively; in no case did addition take place, the behaviour of diphenylnaphthylmethyl in this respect being in marked contrast with that of triphenylmethyl.

Solutions of diphenylnaphthylmethyl are only slowly affected by exposure to light; since, however, the products formed contain considerable quantities of diphenylnaphthylmethane, it seems probable that the reaction occurs on lines similar to those with triphenylmethyl, but far more slowly.

The molecular weight of diphenylnaphthylmethyl has been determined by the cryoscopic method in nitrobenzene, *p*-bromotoluene, *p*-dichlorobenzene, *p*-chlorobromobenzene, and naphthalene respectively, thus giving a temperature range from +6° to 80°; it has been found that the temperature as well as the concentration has a marked influence on the dissociation of free radicles, whilst the nature of the solvent appears to exert but slight influence. Increase in the concentration of the solution invariably causes an increase in the molecular weight, which is interpreted as shifting the equilibrium,  $C_{10}H_7 \cdot CPh_2 \cdot CPh_2 \cdot C_{10}H_7 \rightleftharpoons 2C_{10}H_7 \cdot CPh_2$ , in favour of the bimolecular form. At a temperature of about 60°, diphenylnaphthylmethyl is shown to be present entirely in the unimolecular form, but above this temperature the molecular weight suffers a further decrease, the cause of which has not been established.

H. W.

**The Fluorene Series. I.** ADOLF SIEGLITZ (*Ber.*, 1919, 52, [B], 1513—1517).—Thiele has shown that fluorene condenses with benzaldehyde, anisaldehyde, cinnamaldehyde, and furfuraldehyde in the presence of sodium ethoxide (*A.*, 1900, i, 347; 1906, i, 571). Derivatives of other aldehydes are now described.

9-*o*-Methylbenzylidenefluorene forms flat, colourless needles and prisms, m. p. 109·5°, soluble in concentrated sulphuric acid with violet colour; *picrate*, orange needles, m. p. 138—139°. 9-*p*-Methylbenzylidenefluorene forms flat, colourless crystals, m. p. 97·5°; *picrate*, yellow, m. p. 117—118°. 9:9'-Terephthalylidenedifluorene,  $C_6H_4(CH:C_{13}H_8)_2$ , crystallises in golden-yellow, glistening leaflets, m. p. 209—210°, olive-green in sulphuric acid. The 9-chlorobenzylidenefluorenes are as follows: *ortho*, yellow needles, m. p. 176°, dark brown in sulphuric acid; *meta*, pale yellow prisms and pyramids, m. p. 90·5°, deep green in sulphuric acid; *para*, pale yellow, m. p. 149·5°, deep blue in sulphuric acid. 9-*m*-Bromobenzylidenefluorene forms yellow needles, m. p. 92—93°, deep green in sulphuric acid.

J. C. W.

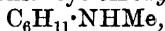
**Transformation of Anilines into cycloHexylamines and the Isomerism of these Bases.** A. SKITA and W. BERENDT (*Ber.*, 1919, 52, [B], 1519—1535).—Hitherto, the catalytic reduction of anilines has given very unsatisfactory results, for there is a great tendency for ammonia to be evolved and secondary amines to result in consequence. With colloidal platinum as the catalyst, however, and by varying the concentration, temperature, and proportion of hydrochloric acid present, it is possible so to control the reduction that the primary cyclohexylamine is the sole product or the secondary base the main product. Reduction with colloidal platinum is about thirty times as rapid as with spongy platinum,



which is probably due, not only to the greater surface available, but to the fact that the bases have no time to "poison" the catalyst before the action is over. In any case, the catalyst must be employed in unusual concentrations, about 0.6% for the monoamines and double this for diamines.

The catalyst is prepared by shaking a solution of hydrochloroplatinic acid, containing gum arabic, with hydrogen, after inoculation with a little colloidal platinum.

The following reductions are described. *Aniline*: A mixture containing 1.5 grams of platinum (from hydrochloroplatinic acid), 1.5 grams of gum arabic, 0.09 mol. (8.37 grams) of aniline, 110 c.c. of glacial acetic acid, and 120 c.c. of water (designated the "normal mixture"), was reduced in three hours at 21°, giving *cyclohexylamine*, b. p. 135° (40.3%), and *dicyclohexylamine*, b. p. 250° (59.7%). At 55–60° the same mixture was reduced in twenty-five minutes, the yield of secondary base being 78.4%. With the addition of 10 c.c. of concentrated hydrochloric acid, the mixture was reduced in two and a-half hours at 21°, giving primary *cyclohexylamine* only. *Alkylanilines*: At about 40–50° good yields of the simple secondary amines are obtained, but at 80°, and with more concentrated solutions of the catalyst, the monoalkylanilines give 40–55% yields of tertiary amines. The dialkylanilines give almost the same results under both conditions. *cycloHexylmethylamine*,



has b. p. 145–147°, and its *benzoyl* derivative has m. p. 85–86°; *cyclohexyldimethylamine* has b. p. 160–161° (A., 1904, i, 661); *cyclohexyldiethylamine* has b. p. 193° (*ibid.*), *dicyclohexylmethylamine* has b. p. 265°, and its lemon-yellow *picrate* has m. p. 140°; *dicyclohexylethylamine* has b. p. 268°, and its *picrate* has m. p. 138°.

*Toluidines*.—The "normal mixture," containing *p*-toluidine, plus 5 grams of hydrogen chloride, was reduced at 25° in four hours, the product being 4-methyl*cyclohexylamine*, b. p. 150–151° (Gutt, A., 1907, i, 508). This is apparently a mixture of *cis*- and *trans*-isomerides, for it yields two *benzoyl* derivatives, the  $\alpha$ -form having m. p. 180° (corr.) (*ibid.*), and the  $\beta$ -form, which is the more soluble of the two in dilute alcohol, having m. p. 116°. At 52° the "normal mixture" is reduced in seventy-five minutes, giving a 68% yield of 4:4'-dimethyldicyclohexylamine, b. p. 133°/10 mm. This gives two *nitrosoamines*, the  $\alpha$ -form, m. p. 128–129° (corr.), crystallising from moderately strong alcohol, and the  $\beta$ -form, m. p. 90–91° (corr.), from more dilute alcohol. With *m*-toluidine the "normal mixture" was reduced in five hours at 23–26°, to 55.6% of primary amine, and 44.4% of secondary base, but at 55° the absorption of hydrogen was complete in thirty minutes, and the yield of secondary amine was 79.1%. 3-Methyl*cyclohexylamine* has b. p. 150–151° (*ibid.*), and forms two *benzoyl* derivatives, the  $\alpha$ -form having m. p. 127° (corr.) and the  $\beta$ -form m. p. 98.5° (corr.). 3:3'-Dimethyldicyclohexylamine has b. p. 172–173° (Wallach, A., 1893, i, 115). In the case of *o*-toluidine the yields with the "normal mixture"

were 83·8% primary and 16·2% secondary amine at 23°, and 58% secondary base at 55°. 2-Methylcyclohexylamine, b. p. 150—151°, hydrochloride, m. p. 269°, forms two *benzoyl* derivatives,  $\alpha$ -, m. p. 146° (corr.) (Gutt, *loc. cit.*), and  $\beta$ -, m. p. 107° (corr.). 2:2'-Dimethyldicyclohexylamine has b. p. 273—274°, forms a *hydrochloride*, m. p. 284°, and yields two *picrates*,  $\alpha$ -, tetrahedra, m. p. 184° (corr.), and  $\beta$ -, delicate needles, m. p. 153° (corr.).

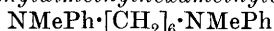
*Nitroanilines*.—*m*-Nitroaniline is mainly reduced to *m*-phenylenediamine if insufficient catalyst is used, but a mixture containing 6·9 grams of base, 4 grams of colloidal platinum, 3 grams of gum arabic, 4 grams of hydrogen chloride, 150 c.c. of glacial acetic acid, and 130 c.c. of water was reduced at 55° so rapidly that heat was developed, and a 62% yield was obtained of cyclohexylene-1:3-diamine, b. p. 193—194°, *platinichloride*, yellow needles (Merling, A., 1894, i, 177). *p*-Nitroaniline, under similar conditions, gave a 45% yield of cyclohexylene-1:4-diamine, b. p. 181°, *platinichloride*, yellow crystals (von Baeyer, A., 1889, 1147).

In most of the reductions the hydrogen is kept under 3 atm. pressure. J. C. W.

**Halogenalkylated Aromatic Amines. IV.** JULIUS VON BRAUN and GEORG KIRSCHBAUM (*Ber.*, 1919, 52, [B], 1716—1724. Compare A., 1918, i, 107, 269, 406).—When methyl- $\beta$ -bromoethylaniline is boiled with hydrochloric acid, it is converted into methyl- $\beta$ -chloroethylaniline,  $\text{NMePh}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ , which is a very pale yellow oil, b. p. 134°/13 mm., and forms a yellow *picrate*, m. p. 107°, a *methiodide*, colourless leaflets, m. p. 125°, and a *p*-nitroso-compound, emerald leaflets, m. p. 69°, which may be oxidised to *p*-nitromethyl- $\beta$ -chloroethylaniline,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ , a greenish-brown, crystalline powder, m. p. 90°, and reduced to methyl- $\beta$ -chloroethyl-*p*-phenylenediamine, an oil which yields an *acetyl* derivative, m. p. 131°. The reactivity of the halogen atom is not so great as in the case of the bromo-derivative, but it is still quite considerable. For example, the base reacts with sodium benzoate to form methyl- $\beta$ -benzoyloxyethylaniline [ $\beta$ -methylanilinoethyl benzoate], m. p. 48—49° (*picrate*, m. p. 164°), and with ethyl sodiomalonate to give ethyl  $\beta$ -methylanilinoethylmalonate,  $\text{NMePh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , a viscous oil, b. p. 190°/mercury pump.

The replacement of one halogen by another may be illustrated still further. The chloro-derivative yields the bromo-compound when boiled with hydrobromic acid, and both may be converted into methyl- $\beta$ -iodoethylaniline, colourless crystals, m. p. 43—44° (*hydriodide*, m. p. 139°), by boiling with hydriodic acid. The phenomenon has been put to practical use in the preparation of a  $\gamma$ -halogenopropyl base. Methylaniline does not react in the desired way with ethylene or trimethylene dichlorides, and the product obtained by heating it with trimethylene dibromide cannot be distilled. By boiling the crude product with hydrochloric acid, however, the above exchange of halogens takes place, and methyl- $\beta$ -

*chloropropylaniline* may be isolated as a very pale yellow oil, b. p. 140—144°/13 mm. This base forms a *platinichloride*, m. p. 154—156°, a *picrate*, m. p. 113°, a *methiodide*, m. p. 107—108°, and a dark, oily *nitroso*-compound, and it reacts with sodium to give oily N:N'-*diphenyldimethylhexamethylenediamine*,

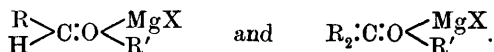


(*picrate*, m. p. 82°), and with trimethylamine to form the oily *quaternary chloride*,  $\text{NMePh} \cdot \text{C}_3\text{H}_6 \cdot \text{NMe}_3\text{Cl}$  (*platinichloride*, m. p. 211°). When boiled with hydrobromic acid, *methyl-β-bromopropylaniline* is formed, and this may now be distilled; b. p. 150—155°/12 mm., 117—121°/0.01 mm.; *picrate*, m. p. 94—95°; *platinichloride*, m. p. 132°.

The halogenoethyl bases yield 1-methyldihydroindole when heated with aluminium chloride, but the halogenopropylanilines do not give quinoline derivatives.

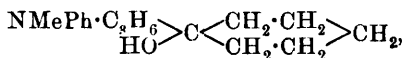
J. C. W.

**Mechanism of the Grignard Reaction.** JULIUS VON BRAUN and GEORG KIRSCHBAUM (*Ber.*, 1919, **52**, [B], 1725—1730).—In the first communication on bromoalkylated anilines (A., 1918, i, 107) it was shown that the magnesium compounds react with aldehydes and ketones, but that the ketones are regenerated on treating the products with water. It was suggested that the primary products can be represented thus:



Apparently, then, when R' is  $\text{NMePh} \cdot \text{CH}_2 \cdot \text{CH}_2-$ , rearrangement into  $\text{RR}'/\text{CH} \cdot \text{O} \cdot \text{MgX}$  is possible in the case of aldehydes, but there are steric hindrances in the way of the formation of  $\text{R}_2\text{R}'\text{C} \cdot \text{O} \cdot \text{MgX}$ . When the heavy NMePh-group is further away, however, as in the case of methyl-γ-bromopropylaniline (preceding abstract), the necessary rearrangement is possible even in the ketone series.

The following compounds are obtained from magnesium γ-methylanilinopropyl bromide: (1) with *isovaleraldehyde*, N:N'-diphenyldimethylhexamethylenediamine (*ibid.*), and *methyl-δ-hydroxy-ζ-methylheptylaniline*,  $\text{NMePh} \cdot \text{C}_3\text{H}_6 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CHMe}_2$ , a viscous oil, b. p. 154—156°/12 mm. (*picrate*, m. p. 161°; *platinichloride*, m. p. 210°); with acetone, methylpropylaniline, and *methyl-δ-hydroxy-δ-methylamylaniline*, a very viscous oil, b. p. 164—170°/13 mm. (*platinichloride*, m. p. 193°); with *cyclohexanone*, the base,



which seems to lose water slowly on heating.

The steric hindrance seems to be connected with the presence of nitrogen also, for the Grignard compound from γ-phenyl-n-butyl bromide (A., 1913, i, 612) behaves quite normally with acetone, yielding *sec*-butylbenzene and βη-diphenyloctane (*ibid.*), but chiefly ε-phenyl-β-methylhexan-β-ol,  $\text{CHMePh} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{OH}$ , a very viscous liquid, b. p. 135°/11 mm.

J. C. W.

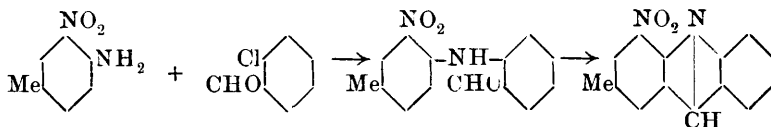
**5-Nitro - 2 - amino - 1 - methyl - 4 - isopropylbenzene.** C. E. ANDREWS (U.S. Pat. 1314923).—To introduce a nitro-group into aminocymene in a position para to the amino-group, the amino-group is first protected against the action of the nitrating medium by boiling with glacial acetic acid for fifteen to twenty hours. Nineteen parts of the solid acetylaminocymene thus obtained are dissolved in 98% sulphuric acid (84 parts) and the solution thus formed is nitrated with a mixture of 98% sulphuric acid (13 parts) and 70% nitric acid (10 parts), while the reacting substances are kept at 0°. By pouring the products into water containing ice a yellow precipitate of *p*-nitroacetylaminocymene is obtained. This may be treated directly for reduction of the nitro- to the amino-group by heating with iron and hydrochloric acid, and the acetyl group may subsequently be removed by treatment with concentrated hydrochloric acid, from which, on keeping, the hydrochloride of 2:5-diamino-1-methyl-4-isopropylbenzene separates as crystals. The intermediate product (5-amino-2-acetyl-amino-1-methyl-4-isopropylbenzene) may be diazotised and coupled with a hydroxy-aromatic compound in alkaline solution, after which the acetyl group can be removed and the 2-amino-group can then be caused to react with hydroxy- or amino-aromatic compounds. This procedure is preferable to reacting on tetrazotised diaminocymene with aromatic hydroxy-derivatives, where two different second components are to be employed in producing bisazo-dyes.

CHEMICAL ABSTRACTS.

**4 - Amino - 5 - methyl - 2 - isopropylbenzenesulphonic Acid.** C. E. ANDREWS (U.S. Pat. 1314927).—Aminocymene or its sulphate is heated for about ten hours with 98% (or fuming) sulphuric acid at about 205° until a test portion gives no reaction for the free amine on making it alkaline. The solid reaction mass is broken up and dissolved in hot sodium hydroxide solution, purified by filtration through "decolorising carbon," and acidified to obtain 4-amino-5-methyl-2-isopropylbenzenesulphonic acid.

CHEMICAL ABSTRACTS.

**Action of *o*-Chlorobenzaldehyde on Chloroanilines and Amines of Fluorene and Anthraquinone.** FRITZ MAYER and IRENE LEVIS (*Ber.*, 1919, **52**, [B], 1641—1652).—It has already been found that under certain conditions *o*-chlorobenzaldehyde does not react with ortho-substituted anilines to form the usual azomethines, but condenses according to the following scheme, taking an actual example (A., 1918, i, 36):



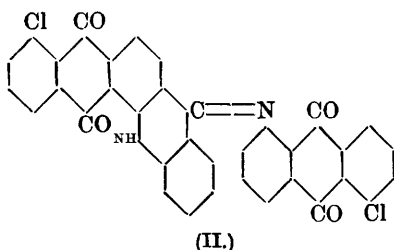
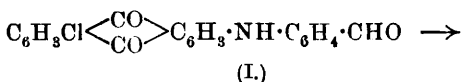
The reaction with chloroanilines and aminofluorenes has now been

examined, but these are found to give only the azomethines or no condensation products at all. Certain anthraquinone derivatives, however, yield the more complex products.

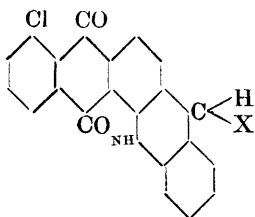
In the experiments, the azomethines were obtained by condensing the components in warm dilute alcohol, and the other condensations were tested by heating the substances in nitrobenzene or naphthalene at 210—220° with a little copper powder and anhydrous sodium carbonate.

The chloroanilines gave the following compounds: 2:2'-*dichlorobenzylideneaniline*, m. p. 112—113°; 3:2'-*dichlorobenzylideneaniline*, two forms, m. p. 104° and m. p. 39—40°, the former passing into the latter on fusion and inoculation with crystals of the low melting form; 4:2'-*dichlorobenzylideneaniline*, m. p. 65—68°, 2:4:2'-*trichlorobenzylideneaniline*, m. p. 97—98°; a *trichloro-2'-chlorobenzylideneaniline*, m. p. 109°, from technical trichloroaniline, the pure 2:4:6-trichloroaniline giving no condensation product. 2-Chloro-4-nitroaniline yields 2:2'-*dichloro-4-nitrobenzylideneaniline*, yellow crystals, m. p. 155—156°. 4-Chloro-2-nitroaniline only reacts in naphthalene solution, and then gives a small yield of 3-chloro-1-nitroacridine, pale yellow needles, m. p. 219—221°. 3-Chloro-*p*-toluidine gives 2:2'-*dichloro-4-methylbenzylideneaniline*, m. p. 68—70°. 2-Chloro-5-nitrobenzaldehyde and *p*-chloroaniline yield 4:2'-*dichloro-5'-nitrobenzylideneaniline*, m. p. 124—125°. 2:4-Dinitroaniline and 1-aminoanthraquinone do not condense with 2-chloro-5-nitrobenzaldehyde. 2-Aminofluorene and 2-aminofluorenone (Diels, A., 1901, i, 521) yield 2:2'-*chlorobenzylideneamino*fluorene, m. p. 128—129, and 2:2'-*chlorobenzylideneamino*fluorenone, m. p. 153—155°. 1-Nitro-2-aminofluorene does not react, but 2-nitro-7-aminofluorene (A., 1902, i, 758) forms 2-nitro-7:2'-*chlorobenzylideneamino*fluorene, m. p. 230°.

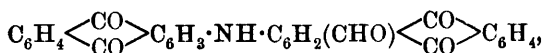
5-Chloro-1-aminoanthraquinone yields *o*-5-chloro-1-anthraquinonylamino benzaldehyde (5-chloro-1-*o*-aldehydoanilinoanthraquinone) (I), reddish-violet crystals, which condenses with more 5-chloro-1-aminoanthraquinone in boiling nitrobenzene, under the influence of mercuric sulphate, giving the compound (II).



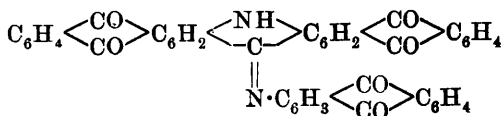
The aldehyde (I) also condenses to the esters of 1:2-*o*-chlorophthalyl-5:10-dihydroacridol (annexed formula), which in the free state is apparently a brownish-violet powder, when heated with sulphuric acid at 115—120°, or with acetic acid saturated with hydrogen chloride. The *hydrogen sulphate* forms dark violet crystals, and the *hydrochloride* is violet.



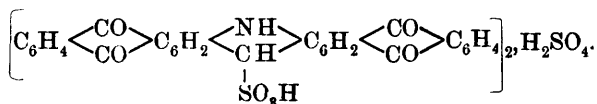
1-Chloroanthraquinone-2-aldehyde (Ullmann, A., 1916, i, 484) condenses with 1-aminoanthraquinone to form 1:1'-*anthraquinonylaminoanthraquinone-2-aldehyde*,



as a violet-red powder, which condenses further with 1-aminoanthraquinone to give a violet *compound* of the formula



Heated with sulphuric acid, the aldehyde also forms the violet *sulphonate* of 1:2:8:9-diphthaloyl-5:10-dihydroacridyl *hydrogen sulphate*,



J. C. W.

**Diphenylamine.** H. ROGERS (U.S. Pat. 1314538).—Diphenylamine is formed by heating a mixture of aniline with about 1% of ammonium bromide in an autoclave, preferably for about forty-eight hours under a condensing column, which is arranged to permit release of the ammonia evolved without loss of aniline. A temperature of about 300° gives the best results. Bromine itself may be used as a catalyst instead of ammonium bromide, or other bromine compounds may be used, for example, aniline hydrobromide, bromobenzene, or magnesium bromide. It is practically essential that about 1% of water should be present in the reaction zone. After heating in the autoclave, the reaction product is fractionated. The first fraction, distilling up to 200°, consists mainly of unchanged aniline, together with a small amount of diphenylamine, and is stored for re-digestion with a fresh amount of catalyst.

The second fraction, distilling at 200—300°, consists of a mixture of aniline with a larger amount of diphenylamine. The larger part of the diphenylamine can be recovered from this second fraction by redistillation. The main quantity of the diphenylamine produced is collected in the fraction which distils at 300° and above. A tarry residue is left in the still, from which the catalyst may be recovered. An apparatus is described. CHEMICAL ABSTRACTS.

### The Isomerism between Real and Pseudo-haloid Salts.

A. HANTZSCH (*Ber.*, 1919, **52**, [B], 1544—1572).—Two distinct chromoisomerides have been found in the case of certain -onium haloids, especially iodides, and a study of their absorption and transformations has led the author to postulate the following characteristics of real and pseudo-haloids. (1) *The genuine haloids*.—The halogen is in ionic union with the -onium complex, that is, is in the "outer sphere" according to Werner's teaching; the salts are optically identical with their ions. Thus,  $[\text{NR}_4]\text{X}$ ,  $[\text{PR}_4]\text{X}$ ,  $[\text{AsR}_4]\text{X}$ ,  $[\text{SR}_3]\text{X}$ ,  $[\text{OR}_3]\text{X}$ . (2) *The  $\psi$ -haloids*.—The halogen is directly united to the central atom; the absorption is much greater than in the case of the normal haloids, and therefore the  $\psi$ -forms are often yellow. They are expressed by the old formulæ for the salts, thus,  $\text{R}_4\equiv\text{N}-\text{I}$ , etc. The tendency for the normal salts to change into the less stable  $\psi$ -forms is favoured by higher temperatures and non-ionising solvents, such as chloroform and *s*-tetrachloroethane, and depends on the nature of the ions. Of the anions, iodine has the greatest effect and chlorine scarcely any. The most effective cations are those in which the central atom is in an unsaturated ring system, as in pyridinium and pyroxonium salts. Next come the most phenylated ions, such as triphenylbenzyl- and triphenylmethyl-phosphonium, but with the alkylated ions, even such as tetrabenzylarsonium, the salts show little tendency to rearrangement. The isomerisation is a time reaction, and therefore a solution in chloroform generally represents an equilibrium, which is displaced not only by rise of temperature, but also by dilution. This suggests participation of the apparently indifferent solvent, and in the case of 1-ethylpyridinium iodide the fact is revealed that both salts form solvates with chloroform, the stable, normal form giving a less stable solvate than the labile  $\psi$ -modification. Ionising solvents have absolutely no optical effect on the normal haloids.

These views are chiefly based on a study of 1-ethylpyridinium iodide and 4-methoxy-2:6-dimethylpyroxonium iodide (compare this vol., i, 72). For the practical details, which are accompanied by much discussion, the original should be consulted.

J. C. W.

### Attempted Preparation of New Compounds of Nitrogen.

H. STAUDINGER and JULES MEYER (*Helv. Chim. Acta*, 1919, **2**, 608—612).—According to Werner's conception, the co-ordination

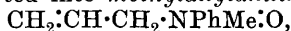
number of nitrogen is four, so that only four atoms or radicles can be united directly to a nitrogen atom. Should it be possible, however, for the nitrogen atom to be united directly with five groups, it is to be expected that the most stable compounds would be formed when the atom is attached to five carbon atoms. The only known compound of this type is triphenylmethyltetramethylammonium,  $\text{CPh}_3\cdot\text{NMe}_4$ , described by Schlenk and Holtz (A., 1916, i, 385), the peculiar instability of which is possibly due to the presence of the triphenylmethyl group. The present communication describes a number of unsuccessful attempts to obtain further compounds of similar structure.

The action of dimethylaniline oxide (2 mols.) on diphenylketen (1 mol.) leads to the formation of dimethylaniline and benzophenone, whilst with molar proportions of the reagents the products are dimethylaniline and diphenylketen oxide, the dimethylaniline oxide behaving in each case as an oxidising agent. With phenylcarbimide and dimethylaniline oxide, carbon dioxide, dimethylaniline, and amorphous substances of high molecular weight are formed. Triethylamine, dimethylaniline, and triphenylamine could not be caused to react with diphenyldiazomethane or with phenylazide.

H. W.

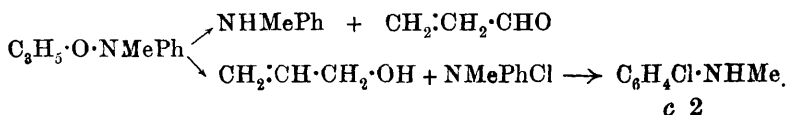
### A Peculiar Transformation of Methylallylaniline *N*-Oxide.

JAKOB MEISENHEIMER (*Ber.*, 1919, **52**, [B], 1667—1677).—Methylallylaniline is converted into *methylallylaniline N-oxide*,



by the action of perbenzoic acid in benzene, being isolated as the *picrate*,  $\text{OH}\cdot\text{NPhMe}(\text{C}_6\text{H}_5)\cdot\text{O}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$ , which crystallises in stout, yellow forms, m. p.  $121^\circ$  (decomp.). If the benzene solution is extracted with 10% hydrochloric acid and the extract is carefully mixed with sodium hydroxide, the oxide is liberated as a very soluble, unstable substance, but if the alkaline solution is heated by means of a current of steam it soon becomes turbid, and a very pale yellow, mobile oil distils over. This oil, b. p.  $97^\circ/14\text{--}16\text{ mm.}$ , is shown to be *N-phenylmethyl-O-allylhydroxylamine*,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{NMePh}$ , by the following series of reactions, but no explanation of its formation from the isomeric methylallylaniline *N*-oxide is offered. The transformation is conditioned by the allyl group, for no other amine oxides are known to behave in this way. The most convenient way to obtain the oil is to oxidise the methylallylaniline with Caro's acid at  $30\text{--}35^\circ$ , extract impurities with ether, and then add concentrated sodium hydroxide and distil in steam.

The oil is hydrolysed by boiling with hydrochloric acid according to the scheme:





Of the products, acraldehyde was identified by its odour and conversion into lead acrylate, methylaniline as its somewhat reddish-yellow *picrate*, m. p.  $144.5^{\circ}$ , and acetyl derivative, *p*-chloromethylaniline as its greenish-yellow *picrate*, m. p.  $153^{\circ}$ , and acetyl derivative (Chattaway and Orton, T., 1901, **79**, 465), and possibly *o*-chloromethylaniline, a *picrate* being obtained in bundles of greenish-yellow needles, m. p.  $133^{\circ}$ . When heated with zinc dust and acetic acid, the oil yields methylaniline and allyl acetate. The latter was hydrolysed, and the alcohol characterised by conversion into *allyl p*-nitrobenzoate, m. p.  $28^{\circ}$ . Reduction by Skita's method (colloidal platinum protected with gum arabic) gives rise to *N*-phenylmethyl-*O*-propylhydroxylamine, an almost colourless oil, b. p.  $92-94^{\circ}/12$  mm., which is hydrolysed by dilute sulphuric acid to propaldehyde, methylaniline, and *p*-hydroxymethylaniline.

J. C. W.

**Action of Nitrous Acid on  $\beta$ -Phenylhydroxylamine.** EUG. BAMBERGER and ALEX. LANDAU (*Ber.*, 1919, **52**, [B], 1837—1842).—A more complete study of this subject, with particular reference to the by-products (compare A., 1894, i, 412). Starting with 79.7 grams of phenylhydroxylamine, 86.5 grams of the nitroso-compound,  $\text{NO}\cdot\text{NPh}\cdot\text{OH}$ , were obtained as a precipitate. The filtrate was extracted with ether, and the aqueous solution added to  $\beta$ -naphthol in sodium hydroxide, giving a quantity of dye corresponding with 2.9 grams of benzenediazonium hydroxide. The ethereal solution was saturated with ammonia gas, filtered (residue A), shaken with 12% ammonia solution (B), dried, and evaporated, leaving 0.69 gram of nitrosobenzene. The residue A consisted of ammonium salts, chiefly of nitrosophenylhydroxylamine, but also of phenylnitroamine,  $\text{NO}_2\cdot\text{NHPh}$ , the latter salt being also present in solution B. The phenylnitroamine was isolated by dissolving A in water, adding sodium carbonate and permanganate in the cold to oxidise the nitrosophenylhydroxylamine to nitrosobenzene, filtering, extracting with ether after acidifying, and shaking the extract with dilute ammonia. On evaporating the ammoniacal solution, 0.11 gram of phenylnitroamine was obtained.

The nitroamine is most probably formed by the rearrangement of the nitrosophenylhydroxylamine under the influence of nitrous acid, for when a solution of the potassium salt of the latter is acidified in the presence of sodium nitrite, a trace of nitroamine is produced.

J. C. W.

**Phenols as Mordant Dyes.** RICHARD MÖHLAU (*Ber.*, 1919, **52**, [B], 1730—1734).—Those phenols which are constitutionally capable of forming internally complex salts are found to impart more or less stable shades to mordanted wool, as the following table indicates:

	Al.	Fe.	Cr.
† $\alpha$ -Anthrol .....	Brown	Brown	Yel.-brown
† $\beta$ -Anthrol .....	Yel.-brown	Yel.-brown	Yel.-brown
Catechol .....	—	*Pale grey	Yel.-grey
1 : 2-Dihydroxynaphthalene.	—	Grey.-brown	Yel.-brown
†1 : 8- „	Black	Brown-black	Brown.-black
†Phenanthraquinol .....	—	—	Red.-brown
1 : 2-Dihydroxyanthracene .	Yel.-brown	Yel.-brown	Yel.-brown
†2 : 3- „	Red.-brown	Red.-brown	Red.-brown
Pyrogallol .....	—	Dark grey	Yel.-grey
Salicylic acid .....	—	*Pale red	—
2 : 3-Dihydroxynaphthoic acid .....	—	*Red.-violet	—
Protocatechuic acid .....	—	*Grey.-violet	Pale grey
Gallic acid .....	—	„	Yel.-grey
Methyl gallate .....	—	„	Pale grey
†1 : 2-Dihydroxynaphthalene-4-sulphonic acid .....	Yel.-brown	Yel.-brown	Red.-brown

(1) With the exception of those marked \*, the colours are unchanged by light and air after thirty days, and also by boiling with 2% soap solution.

(2) Those marked † give colours which are quite stable towards boiling *N*-hydrochloric acid.

No effect is produced by phenol,  $\alpha$ - and  $\beta$ -naphthols, resorcinol, quinol, 1 : 3- and 2 : 7-dihydroxynaphthalenes, or *m*- and *p*-hydroxybenzoic acids.

J. C. W.

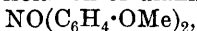
### Acetylation of Nitrophenols in Presence of Catalysts.

G. E. HOFFELMAN (*Proefschrift Delft*, 1919, 134 pp.; from *Chem. Weekblad*, 1919, **16**, 904).—The author has investigated the acetylation of trinitrophenol, *op*-dinitrophenol, *p*-nitrophenol, and *o*-nitrophenol by acetic anhydride both in presence and absence of catalysts such as ferric chloride, zinc chloride, concentrated sulphuric acid, and pyridine. The following points are discussed: (1) The nature of the reactions without a catalyst. (2) Are catalytic reactions definite or does inactivity occur? (3) The relationship between reaction constant and amount of catalyst. (4) The cause of inactivity in certain reactions and the determination of a limit when it occurs. (5) The influence of various catalysts on the acetylation of several nitrophenols. W. J. W.

### Action of Nitric Acid on Phenolic Ethers.

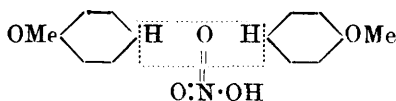
KURT H. MEYER and HANS GOTTLIEB BILLROTH (*Ber.*, 1919, **52**, [B], 1476—1489).—It has been known for some time that by-products with very intense colours are formed during the nitration of phenolic ethers. For example, Decker and Salonina isolated a deep blue compound from thymol ethyl ether (*A.*, 1902, i, 767). It is now shown that the substances can be isolated as perchlorates by diluting the nitration products with ice-water, filtering, and adding the solution to perchloric acid. The salts yield diphenylamine derivatives on reduction, and are best regarded (with Decker) as quinonoid salts of substituted diphenylhydroxylamine-*N*-oxides,  $\text{NPh}_2\text{O}\cdot\text{OH}$ .

This is the derivative of nitric acid which corresponds with diphenylarsinic acid, but attempts to isolate it or its metallic salts have been unsuccessful. In the case of the anisyl derivative, the attempts have led to the isolation of dianisylnitric oxide,



which is more stable than diphenylnitric oxide (Wieland and Offenbächer, A., 1914, i, 955).

In the action of nitric acid on phenolic ethers, there is obviously a choice of two reactions, the ordinary nitration and the present



reaction, represented by the annexed formula. Methyl groups, and especially methoxy-groups, in the meta-position are favourable to this reaction, as they are to

the coupling process with diazo-compounds, but whilst the phenomenon seems to be most characteristic of phenolic ethers, it is not entirely confined to this class, for resorcinol behaves in a similar manner.

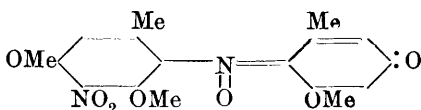
The quinonoid *perchlorate* of *di-p-anisylhydroxylamine N-oxide*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{:O})\text{:C}_6\text{H}_4\cdot\text{O} < \overset{\text{Me}}{\underset{\text{ClO}_4}{\text{C}}}$ , crystallises from acetone on the addition of light petroleum in coppery needles containing  $1\text{H}_2\text{O}$ , which is lost at  $50^\circ$  in a vacuum desiccator. The solutions are red in deep layers and pure blue in thin layers or when very dilute. Reduction to *di-p-anisylamine* may be effected by means of stannous chloride or sodium iodide, and followed titrimetrically in each case. The perchlorate is reduced to *di-p-anisylnitric oxide* by treatment with an alkali, or sodium iodide, or zinc powder, in acetone, or, most conveniently, by dissolving it in pyridine and gradually adding water. The oxide crystallises in needles or platelets, and has the appearance of copper powder, m. p.  $150^\circ$  (decomp.). Its reduction by sodium iodide may be followed volumetrically, and it is re-oxidised to the deep violet salts by bromine or concentrated mineral acids.

Phenetole yields the violet-brown *perchlorate* of diphenetylhydroxylamine *N-oxide*, decomp.  $114^\circ$ , and copper-coloured diphenetyl-nitric oxide. *m*-Tolyl methyl ether gives the *perchlorate* of 5:5'-dimethoxydi-*m*-tolylhydroxylamine *N-oxide*, dark crystals with  $1\text{H}_2\text{O}$ , decomp.  $142^\circ$ . *o*-Tolyl methyl ether gives a mere trace of coloured salt. *m*-5-Xylol methyl ether yields the dark brown *perchlorate* of 5:5'-dimethoxydi-*m*-2-xylolhydroxylamine *N-oxide*.

Resorcinol dimethyl ether gives the *perchlorate* of 2:4:2':4'-tetramethoxydiphenylhydroxylamine *N-oxide*,  $\text{C}_{16}\text{H}_{18}\text{O}_9\text{NCl}_4\cdot\text{H}_2\text{O}$ , as a violet-brown powder, decomp.  $178^\circ$ . The deep green solutions of this become cornflower-blue on adding two equivalents of stannous chloride, and colourless with four equivalents, the final product being 2:4:2':4'-tetramethoxydiphenylamine, which forms large, colourless crystals, m. p.  $71^\circ$ , and yields a *nitroso-derivative*, m. p.  $111^\circ$ . Resorcinol diethyl ether gives the corresponding *perchlorate*,

$C_6H_3(OEt)_2 \cdot N(\cdot O) : C_6H_3(OEt) : OEt \cdot ClO_4$ , in very dark green, glistening needles, decomp.  $131^\circ$ .

Orcinol dimethyl ether yields the *perchlorate* of 3:5:3':5'-*tetramethoxydi-o-tolyldihydroxylamine N-oxide*, dark violet-brown needles,  $1H_2O$ , decomp.  $121^\circ$ , and 3:5:3':5'-*tetramethoxydi-o-tolylamine*, m. p.  $106^\circ$ , and its *nitroso*-compound, m. p.  $186^\circ$ . If



the product of the nitration of orcinol dimethyl ether is left with water, a red compound, decomp.  $150^\circ$ , is deposited, probably represented by the annexed formula.

Phloroglucinol trimethyl ether gives rise to the *perchlorate* of 2:4:6:2':4':6'-*hexamethoxydiphenylhydroxylamine N-oxide*, dark blue crystals, decomp.  $189^\circ$ . J. C. W.

### Aromatic Nitro-derivatives. X. Nitration of Thymol.

M. GIUA (*Gazzetta*, 1919, **49**, ii, 158—166).—The author's investigations on the trinitro-compounds obtained on nitrating thymol and its ethyl and methyl ethers confirm the conclusions of Armstrong and Rennie (*Chem. News*, 1883, **47**, 115), Maldotti (A., 1901, i, 80), and Larter (P., 1901, 183), namely, that Lallemand's trinitrothymol and its ethers (*Compt. rend.*, 1857, **37**, 498; 1857, **38**, 1022; 1860, **43**, 375, 459) are in reality trinitro-*m*-cresol and its ethers.

Further, the trinitro-compound obtained by nitrating either the methyl or the ethyl ether of thymol reacts with hydrazine hydrate in alcoholic solution, giving rise to 2:4:6-trinitro-*m*-tolylhydrazine (compare this vol., i, 100). Phenylhydrazine also reacts with these compounds, yielding the same product (compare this vol., i, 98).

Nitration of the ethyl ether of thymol, dissolved in sulphuric acid, by means of fuming nitric acid at a moderately low temperature and for a short time gives the ethyl ether of dinitro-*m*-cresol, m. p.  $96-97^\circ$  (compare Staedel and Kolb, A., 1891, 186). Further nitration of the latter yields the ethyl ether of 4:5:6-trinitro-*m*-cresol, m. p.  $75^\circ$ . In the ethyl ether of dinitro-*m*-cresol obtained from thymol, one of the nitro-groups occupies the position formerly occupied by the *isopropyl* group, which is evidently eliminated by the action of the nitric acid. T. H. P.

### Transformation of *cyclo*Hexanones into Catechols. GUIDO

CUSMANO (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 30—33).—*Methylisopropylcatechol*,  $C_{10}H_{14}O_2$ , obtained either as such by heating monobromo-Buchu-camphor above its melting point or as diacetyl derivative by heating the same bromo-compound with acetic anhydride and anhydrous sodium acetate in a reflux apparatus, crystallises in colourless prisms, m. p.  $48^\circ$ , b. p. about  $270^\circ$ , gives a green coloration with ferric chloride in alcoholic solution, and in aqueous solution, especially rapidly in presence of alkali,

undergoes oxidation to a hydroxythymoquinone, m. p. about  $165^{\circ}$ ; this oxidation is favoured also by organic bases, such as aniline, which gives a violet-blue coloration. With phenylcarbimide, it yields the crystalline *phenylurethane*,  $C_{24}H_{24}O_4N_2$ , m. p.  $170^{\circ}$ .

T. H. P.

**Molybdic Acid-Catechol Compounds.** R. F. WEINLAND and FRITZ GAISSE (Zeitsch. anorg. Chem., 1919, 108, 231—247).—It has been found that catechol reacts with molybdates in aqueous solution to form coloured compounds in which an atom of the oxygen of the molybdate molecule has been displaced by the catechol residue ( $C_6H_4O_2$ ). The simplest of these compounds is prepared by mixing solutions of ammonium molybdate and catechol, in the proportion of 1 molecule of the former to from 6 to 12 of the latter, and allowing the solution to evaporate, when large, deep red crystals in the form of four- or six-sided columns with sharp pyramidal ends are obtained. They can be recrystallised from water, methyl, or ethyl alcohol, and in each case have the composition represented by the formula  $(NH_4)H[MoO_3(C_6H_4O_2)] \cdot \frac{1}{2}H_2O$ . The aqueous solution is gradually decolorised by acids, and the compound is also decomposed by alkalis. Corresponding salts of the alkali metals could not be prepared, but by the action of pyridine on the ammonium compound two new compounds were obtained, an ammonium pyridine compound, brownish-red needles, easily soluble in water and methyl alcohol, less easily in ethyl alcohol, to which the formula  $(NH_4)(C_5H_5NH)[MoO_3(C_6H_4O_2)] \cdot \frac{1}{2}H_2O$ , is given, and a pyridine salt. The latter can also be prepared by heating an aqueous solution of molybdic anhydride (1 mol.), catechol (1 mol.), and pyridine (2 to 3 mols.). It forms orange-red aggregates of microscopic needles, m. p.  $60^{\circ}$ , and its composition corresponds with the formula  $(C_5H_5N)H_2[MoO_3(C_6H_4O_2)] \cdot 1.5H_2O$ . An anhydrous quinoline salt corresponding in composition with the above ammonium pyridine compound, and a tetramethylammonium compound having the formula  $NMe_4H[MoO_3(C_6H_4O_2)]$  were also prepared. An anhydrous dipyridine salt was also obtained.

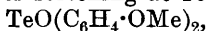
A dipyridine-diccatechol molybdate was obtained from a solution in which one molecular proportion of molybdic acid was heated with two of catechol and five to ten of pyridine. It forms bright red, six-sided tables, and can be recrystallised from methyl alcohol unchanged, but not from water or ethyl alcohol. It has the composition  $(C_5H_5NH)_2[MoO_2(C_6H_4O_2)_2]$ , m. p.  $137^{\circ}$ . In presence of more than two molecular proportions of catechol, the last compound crystallises with the excess of catechol in varying quantities. The compounds isolated contained: (1)  $C_6H_4(OH)_2 \cdot 2H_2O$ , m. p.  $53^{\circ}$ ; (2)  $\frac{1}{2}C_6H_4(OH)_2$ , m. p.  $142^{\circ}$ ; (3)  $1.5C_6H_4(OH)_2 \cdot 2H_2O$ , m. p.  $138^{\circ}$ .

E. H. R.

**m-Anisyltellurium Compounds.** KARL LEDERER (Ber., 1919, 52, [B], 1989—1992. Compare A., 1917, i, 134).—Di-*m*-anisyltelluride has been prepared by the action of magnesium *m*-anisyl iodide on tellurium dibromide; it is purified by conversion into the

crystalline dibromide and reduction of the latter with magnesium methyl iodide.

*Di-m-anisyltelluride*,  $\text{Te}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$ , is a pale yellow oil, b. p. 247—252°/34—36 mm., which gives rise to the following *di-m-anisyltelluronium* compounds in the usual way; *dichloride*, slender, felted needles, m. p. 162—163°; *dibromide*, small, felted needles, m. p. 185—186°; *di-iodide*, minute, golden-yellow needles, m. p. 167—168° (decomp.), after softening at 163°; *oxide*,



amorphous powder, which softens at 69° and is completely molten at 90°; *methiodide*, not obtained in the pure condition. It also forms *additive* compounds with the mercuric haloids as follows: *iodide*,  $\text{Te}(\text{C}_6\text{H}_4\cdot\text{OMe})_2\cdot\text{HgI}_2$ , yellow needles, m. p. 122—123°, after softening at 120°; *bromide*, needles, m. p. 114—115° (decomp.), after softening at 108°; *chloride*, colourless, amorphous powder, which softens at 83° and is completely molten at about 89°.

H. W.

**A Simple and Convenient Way to Prepare Aromatic Selenium Compounds.** A. SCHOELLER (*Ber.*, 1919, 52, [B], 1517—1518).—Instead of treating diazotised anilines with alkali selenides or selenocyanates, which involve the use of hydrogen selenide in their preparation, the same results may be obtained with alkali polyselenides. A reagent is best obtained by fusing black selenium with potassium hydroxide and dissolving the product in ice-water. About twice the theoretical quantity is applied to the diazonium compound, 75% of the excess being precipitated during the reaction and the remainder recovered from the mother liquors of the organic selenide by the action of sulphur dioxide.

Benzenediazonium chloride gives an 80% yield of diphenyl selenide, whilst diazotised anthranilic acid gives a mixture of diselenide (85%) and monoselenide (compare Lesser and Weiss, A., 1913, i, 1184; 1915, i, 445).

J. C. W.

**Cholesterol. XXVIII. Transformation of Cholesterol into Cholanic Acid.** A. WINDAUS and K. NEUKIRCHEN (*Ber.*, 1919, 52, [B], 1915—1919).—It has often been surmised that cholic acid,  $\text{C}_{24}\text{H}_{40}\text{O}_5$ , is intimately connected with cholesterol,  $\text{C}_{27}\text{H}_{46}\text{O}$ , especially as they give similar colour reactions, but a direct proof has necessitated several years of experiment. A clue was first found in the fact that cholesterol yields acetone on oxidation with chromic acid, whereas cholic acid does not, that is, the difference in the carbon content is that of an *isopropyl* group (A., 1918, ii, 22). Cholanic acid,  $\text{C}_{24}\text{H}_{40}\text{O}_2$ , which has the three hydroxyl groups of cholic acid replaced by hydrogen, behaves in the same way (Wieland and Weil, A., 1912, i, 831). This led the authors to attempt the removal of the *isopropyl* group from a suitable cholesterol derivative, and as a substance in which there are no complications left in the nuclear parts of the molecule, they have chosen cholestane,  $\text{C}_{27}\text{H}_{48}$ , the product obtained by the chemical reduction of cholesterol.

When cholestane is oxidised by chromic acid in glacial acetic acid it gives an acid which is remarkably like cholanic acid, but on comparing it with a specimen provided by Wieland it proves to be an isomeride after all. The isomerism is akin to that which exists between cholesterol, dihydrocholesterol, and cholestane on the one hand and coprosterol and  $\psi$ -cholestane on the other, for when  $\psi$ -cholestane is oxidised in the same way the product is the true cholanic acid.

Cholanic acid has m. p.  $164^{\circ}$  and its ethyl ester crystallises in long needles, m. p.  $93-94^{\circ}$ ; *isocholanic acid* has m. p.  $162^{\circ}$  (the mixture begins to soften at  $150^{\circ}$  and is clear at  $155^{\circ}$ ), the *methyl* ester has m. p.  $79-80^{\circ}$ , and the *ethyl* ester crystallises in leaflets, m. p.  $79^{\circ}$ . J. C. W.

**Xanthosterol, a Crystalline Compound from the Bark of *Xanthoxylum Budrunga*.** H. DIETERLE (*Arch. Pharm.*, 1919, **257**, 260—263).—*Xanthosterol*,  $C_{23}H_{40}O$ , obtained in about 0.25% yield by extracting the bark of *Xanthoxylum Budrunga* with light petroleum, forms slender, white needles, m. p.  $213-214^{\circ}$ . Its molecule contains a hydroxyl group, and it forms a *benzoyl* derivative,  $C_{30}H_{44}O_2$ , fine needles, m. p.  $264-265^{\circ}$ ; an *ethylcarbonato*-derivative,  $C_{23}H_{39}O \cdot CO_2Et$ , white, nodular crystals, m. p.  $175-176^{\circ}$ ; a *methylcarbonato*-derivative,  $C_{23}H_{39}O \cdot CO_2Me$ , greasy leaflets, m. p.  $191-193^{\circ}$ ; and a *bromo*-derivative,  $C_{23}H_{39}OBr$ , colourless needles, m. p.  $169-170^{\circ}$ .

Its reactions indicate xanthosterol to be an alcohol related to lupeol (compare Likiernik, A., 1891, 551, 1446; Sack and Tollens, A., 1904, i, 1011) and to alstol (Sack and Tollens, *loc. cit.*). With concentrated sulphuric acid, it yields a yellow coloration, which changes to brown with a slight green fluorescence on heating. When its chloroform solution is treated with concentrated sulphuric acid, the chloroform gradually becomes pale yellow with a green fluorescence and the acid brown; evaporation of this chloroform solution leaves a violet residue. Addition of concentrated sulphuric acid, drop by drop, to a solution of xanthosterol in acetic anhydride gives a stable, red coloration.

The bark of *Xanthoxylum Budrunga* contains also an alkaloid, to be studied later. T. H. P.

**Condensation of Formaldehyde with some Unsaturated Compounds.** H. J. PRINS (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 51—56. Compare A., 1917, i, 685; 1918, i, 261).—The condensation of formaldehyde with styrene, anethole, camphene, and cedrene has been studied. The reaction with styrene yields  $\beta$ -phenyltrimethylene glycol (*loc. cit.*), b. p.  $176^{\circ}/13$  mm.,  $D_4^{15}$  1.1161,  $n_D^{19}$  1.54267, and its *methylene ether*, b. p.  $128-130^{\circ}$ ,  $D_4^{18}$  1.1111,  $n_D^{18}$  1.53063. Anethole yields the *methylene ether* of *p*-methoxyphenylbutylene glycol, b. p.  $168-170^{\circ}/13$  mm.,  $D_4^{16}$  1.1197,  $n_D^{16}$  1.53438. On boiling a solution of trioxymethylene in acetic acid with camphene for three days, *homocamphenol ace*-

*tate* is produced, an oil, b. p. 124—128°/13 mm.,  $D_4^{19}$  1.0013,  $n_D^{19}$  1.48209. A mixture of cedrene with an equivalent quantity of formaldehyde in 15% sulphuric acid and acetic acid on stirring for three days yields *homocedrenol*, b. p. 168—171°/13 mm.,  $D_4^{19}$  1.0270,  $n_D^{19}$  1.51826, along with products of considerably higher boiling point.

J. F. S.

**Manufacture of Synthetic Drugs [Adrenaline].** NANAYOSHI NAGAI (Brit. Pat. 118298).—Equimolecular proportions of nitromethane and diacetylprotocatechualdehyde, prepared by the interaction of protocatechualdehyde and acetyl chloride or acetic anhydride, are condensed at ordinary temperatures in presence of a dilute solution of a weak alkali to diacetoxyphenylnitroethanol,  $C_6H_3(OAc)_2 \cdot CH(OH) \cdot CH_2 \cdot NO_2$ . The crystalline product is collected, washed free from protocatechualdehyde with ether, and treated with acetic acid and zinc dust in presence of a 35% formaldehyde solution containing a molecular equivalent of formaldehyde, whereby simultaneous reduction and methylation take place with the production of diacetoxyphenylmethylaminoethanol,  $C_6H_3(OAc)_2 \cdot CH(OH) \cdot CH_2 \cdot NHMe$ . The zinc is precipitated from the reaction mixture as sulphide, and to the filtered solution the requisite amount of hydrochloric acid is added to effect hydrolysis and to combine with the liberated base. On evaporation at a low temperature in a vacuum, crystals of dihydroxyphenylmethylaminoethanol hydrochloride (adrenaline hydrochloride) are obtained.

G. F. M.

**Benzoylation of some Hydroxy- or Amino-aromatic Compounds.** FRÉDÉRIC REVERDIN (*Helv. Chim. Acta*, 1919, 2, 729).—The author has recently succeeded in effecting certain difficult benzoylations by benzoyl chloride in the presence of a little concentrated sulphuric acid (A., 1918, i, 536); the latter substance has been employed previously for benzoylation with benzoic anhydride.

H. W.

**Manufacture of  $\beta$ -Halogen-ethylaminobenzoic Acid Esters.** SOCIÉTÉ CHIMIQUE DES USINES DU RHONE (Brit. Pat. 128553).— $\beta$ -Halogen-ethyl-*p*-aminobenzoic esters of the general formula  $XCH_2 \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot CO_2R$ , where X is a halogen and R an alkyl group, are obtained by treating the corresponding hydroxyethyl compounds (Brit. Pat. 128552) with halogenating agents, such as phosphorus or sulphur haloids, thionyl chloride, or bromide, etc., preferably in the presence of a diluent such as benzene or a tertiary amine. *Ethyl  $\beta$ -chloroethyl-*p*-aminobenzoate* is a crystalline substance, melting at 69°, and boiling at 183° at 3 mm. pressure. [See also *J. Soc. Chem. Ind.*, 1920, 43A.]

G. F. M.

**Manufacture of  $\beta$ -Alkylaminoethylaminobenzoic Alkyl Esters.** SOCIÉTÉ CHIMIQUE DES USINES DU RHONE (Brit. Pat. 128554).— $\beta$ -Alkylaminoethyl-*p*-aminobenzoic esters are obtained by heating for several hours in a closed vessel at a temperature of

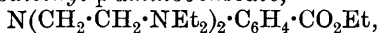


about 100° a mixture of an alkylamine and a  $\beta$ -halogenethyl-*p*-aminobenzoic ester (see preceding abstract). *Ethyl  $\beta$ -diethylaminobenzoate*,  $\text{NEt}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et}$ , prepared thus from diethylamine and ethyl  $\beta$ -chloroethyl-*p*-aminobenzoate, is an oil giving a water-soluble *monohydrochloride* when evaporated to dryness with the requisite quantity of dilute hydrochloric acid. On recrystallisation from alcohol the hydrochloride gives white needles melting at 156°.

G. F. M.

### Manufacture of Substituted Benzoic Acid Esters.

SOCIÉTÉ CHIMIQUE DES USINES DU RHONE (Brit. Pat. 128912).—Di- $\beta$ -halogen-ethyl-*p*-aminobenzoic acid esters of the general formula  $\text{N}(\text{CH}_2\text{CH}_2\text{X})_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{R}$ , where X is a halogen and R an alkyl group, are prepared in the same way as the monohalogen esters (see Brit. Pat. 128553, preceding page), starting from the di- $\beta$ -hydroxyethylaminobenzoic esters (see Brit. Pat. 128552). *Ethyl di- $\beta$ -chloroethyl-*p*-aminobenzoate* melts at 53° and boils at 215°/3 mm. with slight decomposition. By the method described in Brit. Pat. 128554 (preceding abstract) the dichloro-esters may be converted into di- $\beta$ -alkylaminoethyl-*p*-aminobenzoic esters. Thus diethylamine and ethyl di- $\beta$ -chloroethylaminobenzoate give *ethyl tetraethyldiaminodiethyl-*p*-aminobenzoate*,



which forms a crystalline mass, soluble in dilute hydrochloric acid to give a dihydrochloride; this on crystallisation from alcohol forms white needles, m. p. 194—195°.

G. F. M.

### Some Derivatives of *p*-Dimethylaminobenzoic Acid.

H. RIVIER and CH. SCHNEIDER (*Helv. Chim. Acta*, 1919, 2, 717—719).—*Ethyl p*-dimethylaminobenzoate crystallises in colourless leaflets, m. p. 67—68°. *p*-Dimethylaminobenzanilide has m. p. 181—182° (compare Staudinger and Endle, A., 1917, i, 646), and is converted by phosphorus pentachloride into the *hydrochloride* of *p*-dimethylaminobenzanilide *iminochloride*,  $\text{NPh} \cdot \text{CCl} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2 \cdot \text{HCl}$ . *p*-Dimethylaminothiobenzanilide, from the anilide and phosphorus pentasulphide, forms yellow needles, m. p. 170—171°.

H. W.

**The Replacement of Halogen attached to a Ring Carbon Atom by other Substituents. I. Replacement of Halogen by the Carboxyl Group.** KARL W. ROSENMOND and ERICH STRUCK (*Ber.*, 1919, 52, [B], 1749—1756).—Halogen atoms in aromatic compounds can be directly replaced by carboxyl groups by heating the compounds with aqueous or aqueous-alcoholic potassium cyanide and a little cuprous cyanide for some hours at about 200° in strong, sealed tubes. Good results have been obtained with halogen derivatives of benzene (mono- and di-), toluene, aniline, nitrobenzene, phenol, carboxylic acids, naphthalene, and thiophen. Apparently, copper is the unique catalyst in such condensations, for in the well-known and easier case of the replacement of halogen by the amino-group, silver, nickel, cobalt, zinc, and cadmium salts are almost ineffective.

The following examples are given. Benzoic acid from bromobenzene, *p*-toluic acid from *p*-bromotoluene, *p*-aminobenzoic acid from *p*-bromoaniline, terephthalic acid from *p*-dibromobenzene, anisic acid from *p*-bromoanisole, the three phthalic acids from the three bromobenzoic acids,  $\alpha$ -naphthoic acid from  $\alpha$ -bromonaphthalene, thiophen-2-carboxylic acid from 2-bromothiophen, and *o*-3:4-dimethoxybenzoylbenzoic acid,  $C_6H_3(OMe)_2 \cdot CO \cdot C_6H_4 \cdot CO_2H$ , small needles, m. p. 208—209°, from 2-bromo-3':4'-dimethoxybenzophenone (*o*-bromobenzoylveratrole), stout plates, m. p. 154—155°, this being obtained by the Friedel and Crafts's reaction.

The behaviour of chloronitrobenzenes towards potassium cyanide was investigated by Richter (1871—1873), who found that the meta- and para-compounds gave chlorobenzoic acids when heated with the cyanide solutions at 200° whereas *o*-chloronitrobenzene was unaffected. It is now found that the last isomeride yields *o*-nitrobenzoic acid if a little cuprous cyanide is present and the temperature is not allowed to rise above 195°, whereas at about 210° phthalic acid and another substance, free from nitrogen and chlorine, are the products.

J. C. W.

#### Preparation of Tyrosine for the Tyrosinase Reaction.

M. W. BEIJERINCK (*Chem. Weekblad*, 1919, **16**, 1494—1495).—A small quantity of trypsinum activum is added to a 10% solution of pepton siccum, the mixture being put in a stoppered flask and shaken with a little chloroform to prevent decomposition by anaërobie bacteria. The flask is kept in a thermostat at 40°, with occasional agitation. After ten to fourteen days the peptone will be converted into tyrosine. *Euphorbia lathyris*, *Beta vulgaris*, *Morus nigra*, and *Microspira tyrosinatica* are recommended as sources of tyrosinase.

W. J. W.

**Intra- and Inter-molecular Active Forces and their Significance in Atomic Rearrangements, in Racemisation, and in Asymmetric Synthesis.** EMIL ERLÉNMEYER (*Biochem. Zeitsch.*, 1919, **97**, 198—245).—On reducing active phenylbromolactic acid with zinc in hot alcoholic solution one half of it passes into phenyl- $\beta$ -lactic acid and the other half into cinnamic acid. When the zinc salts of the acids are decomposed with dilute sulphuric acid and the cinnamic acid is extracted with ether, it is found to be optically active, rotating in the same direction as the active phenylbromolactic acid from which it is derived. That this activity of the cinnamic acid is not due to contamination with phenyl-lactic acid is shown by experiments in which repeated extractions with water still leave an active cinnamic acid. This is further confirmed by the fact that a mixture of *i*-cinnamic acid with active phenyl-lactic acid of the same optical activity as that shown by the active cinnamic acid differs from it in other respects. The active cinnamic acid obtained as above shows an asymmetric crystalline form. On brominating a mixture of the zinc salts of *d*-phenyl-lactic acid and *i*-cinnamic acid the *l*-dibromide of cinnamic acid is obtained. On the other hand, *l*-phenyl-lactic acid and *i*-cinnamic

acid yield the *d*-dibromide. The reduction products of *l*- and *d*-phenylbromolactic acids, likewise, yield dibromides of cinnamic acid of the opposite rotation to the phenylbromolactic acids employed. Further experiments with *d*-tartaric acid, *l*-chlorosuccinic acid, *l*-mandelic acid, and *i*-cinnamic acid have shown the following:—

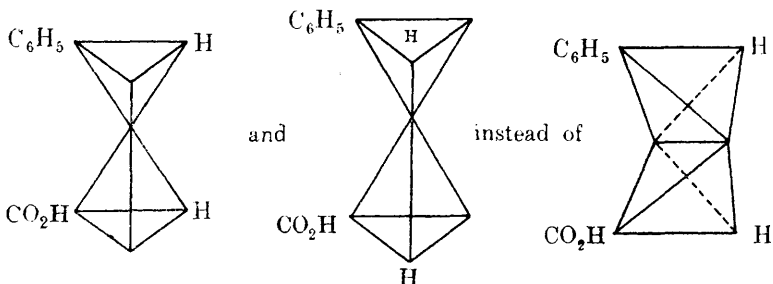
*i*-Cinnamic acid with *d*-tartaric acid yields *l*-cinnamic acid +  $\text{Br}_2 \rightarrow d$ -dibromide.

*i*-Cinnamic acid with *l*-chlorosuccinic acid yields *d*-cinnamic acid +  $\text{Br}_2 \rightarrow l$ -dibromide.

*i*-Cinnamic acid with *l*-mandelic acid yields *d*-cinnamic acid +  $\text{Br}_2 \rightarrow l$ -dibromide.

On treating *d*-cinchonine with *i*-cinnamic acid, *l*-cinnamic acid is obtained, and on bromination the *d*-dibromide is formed.

As the geometrical isomeric formula of cinnamic acid with the double bond cannot account for the active cinnamic acids, the author suggests a stereoisomeric structure with free unsaturated affinities thus:



He also suggests that the activation of the cinnamic acid in the above reactions is brought about by the "induction" influence of the asymmetric active components involved in the reactions, namely, the phenyl-lactic acids, *d*-tartaric acid, *l*-chlorosuccinic acid, etc.

The stereoisomerism of the optically active *isovaleric* acid obtained by the author and Landsberger from the brucine salt of methyl-ethylmalonic acid is also discussed.

S. S. Z.

**The Explanation of the Reciprocal Action of Asymmetric Substances with an Asymmetric Carbon Atom on Cinnamic and *allo*-Cinnamic Acids as Based on the Author's Isomerism Theory of the Ethylene Derivatives.** EMIL ERLÉNMEYER (*Biochem. Zeitsch.*, 1919, **97**, 245—255).—Applying the theory advanced in the preceding paper, the author discusses the action of some asymmetric substances on cinnamic and *allo*-cinnamic acids. The stereoisomeric formulæ of storax- $\alpha$ -cinnamic acid, storax- $\beta$ -cinnamic acid, triclinic cinnamic acid, *allocinnamic* acid, *isocinnamic* acid (Liebermann), and *isocinnamic* acid (Erlénmeyer, sen.) are discussed.

S. S. Z.

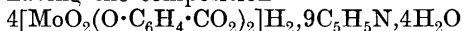
**Walden's Inversion.** EMIL ERLÉNMEYER (*Biochem. Zeitsch.*, 1919, **97**, 255—261).—A theoretical paper. Walden's inversion is discussed in the light of the author's "induction" theory described in the preceding abstracts. S. S. Z.

**Concerning the Force Emanating from Asymmetric Molecules and its Significance in Biochemistry.** EMIL ERLÉNMEYER (*Biochem. Zeitsch.*, 1919, **97**, 261—311).—A theoretical paper. A lengthy exposition of the author's theory as to the stereoisomerism of ethylene derivatives and the "induction" influence of asymmetric active compounds (see preceding abstracts). Many observations already made in stereochemistry and biochemistry are discussed in the light of the new hypotheses.

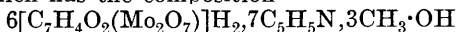
S. S. Z.

**Compounds of Molybdic Acid with Aromatic *o*-Hydroxy-Acids (Salicylic Acid and  $\alpha$ -Hydroxynaphthoic Acid).** R. F. WEINLAND and KURT ZIMMERMANN (*Zeitsch. anorg. Chem.*, 1919, **108**, 248—266).—It has been found that salicylic acid and  $\alpha$ -hydroxynaphthoic acid combine with molybdic acid to form a series of coloured complex compounds. The complex acids themselves could not be isolated, but a number of pyridine, quinoline, and tetramethylammonium salts were prepared in crystalline condition. No compounds are formed between molybdic acid and *m*- or *p*-hydroxybenzoic acids. The evidence indicates that only the hydroxy-group of the organic acid interacts with the molybdic acid, not the carboxyl group.

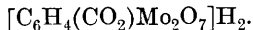
By heating together in aqueous solution molybdic anhydride, salicylic acid, and pyridine in the molecular proportions 1:7:7, a deep yellow salt crystallising in thick, irregular, six-sided tables was obtained having the composition



(No. 1). When prepared in methyl-alcoholic solution, the same salt was obtained anhydrous. It cannot be recrystallised unchanged. Quinoline and tetramethylammonium salts of the same complex acid were prepared, and were all yellow. The corresponding pyridine salt containing  $\alpha$ -hydroxynaphthoic acid is yellow. This is a complex acid salt containing 15 molecules of hydroxynaphthoic acid to 7 of molybdic acid and 13 of pyridine (No. 5). When this is heated with methyl alcohol, it is changed into the normal salt,  $\text{MoO}_2(\text{O} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CO}_2)_2(\text{H} \cdot \text{C}_5\text{H}_5\text{N})_2, 5\text{H}_2\text{O}$  (No. 6). When the compound No. 1 is heated with methyl alcohol, a new compound crystallises which has the composition



(No. 11). This compound contains the new acid,

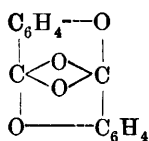


The same anion appears to be present in a flesh-red compound which is formed by heating the pyridine salt No. 1 with water, and has the formula  $8[\text{C}_7\text{H}_4\text{O}_2(\text{Mo}_2\text{O}_7)]\text{H}_2, 9\text{C}_5\text{H}_5\text{N}$  (No. 10). A similar flesh-coloured salt is obtained when No. 11 is heated in water; this has the composition  $[\text{C}_7\text{H}_4\text{O}_2(\text{MoO}_3)_2]\text{C}_5\text{H}_5\text{N}, \text{H}_2\text{O}$  (No. 12). By

heating the salt No. 5 with water, a yellowish-grey compound is obtained having the composition  $[C_{11}H_6O_2(MoO_3)_2]_3C_5H_5N$  (No. 13).

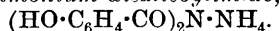
Sodium, potassium, and ammonium salts of salicylomolybdic acid were also prepared. These were brownish-red compounds of very complex constitution, and appear to be double salts of mono-salicylomolybdic acid,  $[MoO_3 \cdot O \cdot C_6H_4 \cdot CO_2]H_2$ , and disalicylomolybdic acid,  $[MoO_2(O \cdot C_6H_4 \cdot CO_2)_2]H_2$ .  
E. H. R.

**A New Disalicylide.** RICHARD ANSCHUTZ [with HANS JANSEN, ALFRED LUBLIN, and GEORG METZGES] (*Ber.*, 1919, **52**, [B], 1875—1895).—By the distillation of *o*-acetoxybenzoic acid under less than 20 mm. pressure, the author has obtained Einhorn and Pfeiffer's disalicylide, m. p.  $200^\circ$  (A., 1901, i, 712), and a new isomeride, m. p.  $213^\circ$ , which is less soluble in chloroform than the old one. It is found that the new isomeride, designated *α*-disalicylide (small, glistening prisms, m. p.  $213^\circ$ ), is the normal disalicylide of the formula  $C_6H_4 \begin{smallmatrix} \diagup O \cdot CO \\ \diagdown CO \cdot O \end{smallmatrix} C_6H_4$ , whereas the older, *β*-disalicylide, is probably represented by the annexed formula.

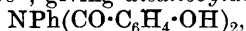


When distilled under reduced pressure, each passes to a slight extent into the other, but under atmospheric pressure they both give xanthone and carbon dioxide. Several other salicylic acid derivatives give the same pair of disalicylides when carefully distilled under reduced pressure, namely, tetrasalicylide, polysalicylide, diposal (salicylsalicylic acid), acetyldiposal (*o*-2-acetoxybenzoyloxybenzoic acid, D.R.-P. 236196), and 2:2'-diacetoxybenzoic anhydride (from aspirin, by the action of thionyl chloride and pyridine, D.R.-P. 201329).

The *α*-disalicylide reacts with boiling alcohols to give the esters of diposal; *methyl o*-2-hydroxybenzoyloxybenzoate (*methyl salicylsalicylate*),  $OH \cdot C_6H_4 \cdot CO \cdot O \cdot C_6H_4 \cdot CO_2Me$ , has m. p.  $86\text{--}87^\circ$ , and the *ethyl* ester, m. p.  $59^\circ$ , agreeing with specimens made by the action of alcoholic hydrogen chloride on diposal. The *β*-disalicylide is much more stable towards alcohols. When heated with methyl alcohol at  $150^\circ$  for six hours, it is partly converted into methyl salicylate. Similarly, the *α*-isomeride reacts with ammonia in chloroform solution about five times as fast as the *β*-form, giving the ammonium disalicylimide,



This is a canary-yellow powder which may be obtained from methyl salicylate, through the amide and imide (Schulerud, A., 1881, 42). The ammonium salt has been converted into the following salts: *silver*,  $(HO \cdot C_6H_4 \cdot CO)_2N \cdot Ag$ ; *calcium*,  $CaX_2 \cdot 2H_2O$ ; *strontium*,  $SrX_2 \cdot 3H_2O$ ; *barium*,  $BaX_2 \cdot H_2O$ ; *mercuric*,  $HgX$ ; *cupric*,  $CuX$ ; and *lead*,  $PbX$ . *α*-Disalicylide also reacts with aniline and *p*-toluidine at about  $100^\circ$ , giving *disalicylanilide*,



m. p.  $165^\circ$ , and *disalicyl-p-toluidide*, m. p.  $149^\circ$ .

J. C. W.

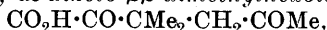
**Isomerism of [Methyl] *o*-Benzoylbenzoate.** A. HANTZSCH (*Ber.*, 1919, 52, [B], 1572—1573).—McMullen (A., 1916, i, 560) doubted the existence of isomerism in the case of methyl *o*-benzoylbenzoate because he could not obtain the  $\psi$ -form described by Meyer (A., 1904, i, 747). Hantzsch points out that he was successful in isolating this isomeride (A., 1916, i, 399). J. C. W.

**Oxidative Degradation of Dehydroisofenchoic Acid [Dehydroisofenchocamphoric Acid].** N. J. TOIVONEN (*Annalen*, 1919, 419, 176—216).—The experiments were originally undertaken with the object of elucidating the composition of dehydroisofenchoic acid; meanwhile, this has been accomplished by other methods (compare Aschan, A., 1913, i, 198), and the paper mainly gives an account of an instance of abnormal oxidation by permanganate in alkaline solution.

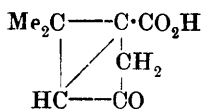
*dl*-Dehydroisofenchoic acid was prepared by the successive action of phosphorus pentachloride and bromine on *dl*-isofenchoic acid, conversion of the product into the ethyl ester, removal of hydrogen bromide from the latter by means of quinoline, and subsequent hydrolysis; it has m. p. 190—191°, and is soluble in water at 25° to the extent of 0.1061 gram in 100 grams. The ethyl ester has b. p. 131—134°/9—10 mm., 260—262°/772 mm.,  $D_4^{20}$  1.0121,  $n_D^{20}$  1.45738. The monoethyl ester ( $\beta$ -form?) is a colourless, viscous liquid, b. p. 168—171°/9 mm.,  $D_4^{20}$  1.0730, whilst a second modification ( $\alpha$ -form?) has b. p. 178—180°/15 mm., m. p. 50—51°,  $D_4^{20}$  1.0737,  $n_D^{20}$  1.47232. Attempts to convert the acid into an anhydride by means of acetyl chloride were unsuccessful, and it was not isomerised by a mixture of glacial acetic and hydrochloric acids (D 1.2). It did not unite with bromine. Hydrogen bromide, on the other hand, readily combined with it, yielding an acid,  $C_{10}H_{15}O_4Br$ , m. p. 267° (decomp.), which was not dehydrated by acetyl chloride, and, on energetic reduction, gave *r-cis-iso*-fenchoic acid. (The investigation of this action is not yet completed.) *d*-Dehydroisofenchoic acid, prepared similarly to the *dl*-acid, forms monoclinic needles and leaflets, m. p. 170—171°,  $[\alpha]_D^{17.5} + 30.28^\circ$  in alcoholic solution, and is soluble in water to the extent of 0.3761 gram in 100 grams at 25°. The diethyl ester is a colourless, mobile liquid, b. p. 123°/6 mm., 261—262°/772 mm.,  $D_4^{20}$  1.0130,  $n_D^{21}$  1.45892,  $[\alpha]_D^{23} + 36.69^\circ$ . The monoethyl ester ( $\beta$ -form?) has b. p. 164°/8 mm.,  $D_4^{20}$  1.0760,  $n_D^{21}$  1.46931,  $[\alpha]_D^{20} + 40.26^\circ$ , whilst the corresponding  $\alpha$ -variety (?) has b. p. 169—170°/8 mm., m. p. 46—47°,  $[\alpha]_D^{19} + 19.71^\circ$  in alcoholic solution. *l*-Dehydroisofenchoic acid has m. p. 170—171°,  $[\alpha]_D^{20} - 30.43^\circ$  in alcohol, and dissolves in water to the extent of 0.3735 gram in 100 grams at 25° (*diethyl* ester, colourless, mobile liquid, b. p. 140—143°/10 mm., 262—263°/772 mm.,  $D_4^{20}$  1.0145,  $n_D^{19}$  1.45709,  $[\alpha]_D^{19} - 36.18^\circ$ ; *monoethyl* ester, [ $\beta$ -form], colourless, almost odourless, viscous liquid, b. p. 172—175°/10 mm.).

When a faintly alkaline solution of dehydroisofenchoic acid is oxidised by potassium permanganate (1%) at 0°, about two atoms

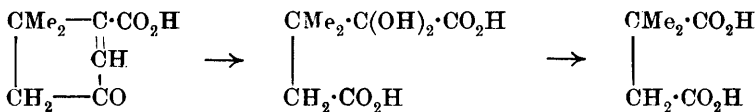
of oxygen are absorbed, and the syrupy product appears to consist mainly of a *lactonic acid*, which could not be isolated in the pure condition. At ordinary temperatures under the same conditions, oxidation proceeds until rather more than four atoms of oxygen have been used, and the product is a crystalline acid,  $C_8H_{10}O_3$  (see later). If, however, a brisk current of carbon dioxide is passed through the mixture during oxidation and an excess of acid is immediately added,  *$\alpha\delta$ -diketo- $\beta\beta$ -dimethylhexoic acid*,



is obtained as a colourless, viscous liquid, which can be neither caused to crystallise nor distilled, even under diminished pressure. It does not appear to react normally with phenylhydrazine or semicarbazide, but its constitution follows from its oxidation by hydrogen peroxide to mesitonic acid,  $CO_2H \cdot CMe_2 \cdot CH_2 \cdot COMe$ , m. p.  $75^\circ$  (*semicarbazone*, m. p.  $197.5^\circ$  [decomp.], phenylhydrazone, m. p.  $135^\circ$ ). The acid is converted by boiling dilute solutions of alkali hydroxides into the acid,  $C_8H_{10}O_3$ , which is identical with the substance described by Perkin, Thorpe, and Walker (T., 1901, 79, 729), to which they ascribed the annexed formula. It has m. p.  $180^\circ$  (*semicarbazone*, m. p.  $255^\circ$ , phenylhydrazone, yellow needles, m. p.  $222^\circ$ , *methyl ester*, colourless, moderately mobile liquid, b. p.  $112-113^\circ/14$  mm.,  $D_4^{20}$  1.0783,  $n_D^{18.5}$  1.47860). It is converted by bromine in acetic acid solution into a *dibromo-acid*,



$C_8H_{10}O_3Br_2$ , shining, rhombic leaflets, m. p.  $164^\circ$ , which, on reduction with zinc dust and acetic acid, yields dimethylcyclopentanone-carboxylic acid, m. p.  $104^\circ$ , which is also obtained by reduction of the acid,  $C_8H_{10}O_3$ , itself (compare Perkin, Walker, and Thorpe, *loc. cit.*). When oxidised by permanganate in alkaline solution, it yields  *$\alpha\alpha$ -dihydroxy- $\beta\beta$ -dimethylglutaric acid*, m. p.  $85^\circ$  (which, when preserved in a vacuum desiccator, readily passes into  *$\alpha$ -keto- $\beta\beta$ -dimethylglutaric acid*, m. p.  $99^\circ$ ), and  *$\alpha\delta$ -dimethylsuccinic acid*. The author doubts the correctness of the formula ascribed to the acid,  $C_8H_{10}O_3$ , by Perkin, Walker, and Thorpe, and prefers to regard it as 5:5-dimethyl- $\Delta^1$ -cyclopenten-3-one-1-carboxylic acid, its oxidation occurring in accordance with the scheme:



H. W.

**The Derivation of Valency Laws. The Principle of Cationic Partial Valencies.** HUGO KAUFFMANN (*Ber.*, 1919, 52 [B], 1422—1435).—In connexion with the problem of halochromism, it has already been shown that the basic functions of the dye and the colour of its salts do not always run parallel. In the case of some dimethoxy-derivatives of triphenylcarbinol, for example, it

has been found that whereas the 2:4-compounds are more basic than the 3:4-, and these much more so than the 2:5-isomerides, the latter give the deepest coloured salts. That is, resorcinol derivatives give the strongest bases, but quinol derivatives the most deeply coloured salts (A., 1914, i, 39). The principle may be established, therefore, that two auxochromes have the greatest effect on a chromogen when they are in the para-position to each other. This principle has already been tested in the case of benzene derivatives having the auxochrome and chromophore in the same ring (A., 1906, i, 841; 1911, i, 368, 930; 1912, i, 863), but now, in order to throw light on the triphenylcarbinol salts, it has been examined in the case of some compounds in which the chromophore is connected by a carbon chain to the nucleus. The methoxyl group is chosen as the auxochrome, to avoid complications such as quinonoid isomerism and betaine-like salt formation. As the following table shows, the 2:5-isomerides have the deepest shades of colour.

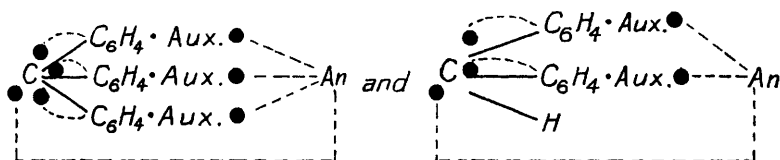
Chromophore.	2:5-.	3:4-.	2:4-.
CH:CH-NO <sub>2</sub> .....	Orange-red	Yellow	Yellow
CH:CMe-NO <sub>2</sub> .....	Orange	Pale yellow	Yellow
CH:CPh-NO <sub>2</sub> .....	Orange	Lemon-yellow	Yellow
CH:CPh-CO <sub>2</sub> H .....	Pale yellow	White	White
CH:CPh-CN .....	Yellow	White	Pale yellow
CH:C(CN)-CO <sub>2</sub> Et.....	Yellow or orange	White	Greenish-yellow
CH:C(CN)-CN .....	Golden-yellow	Pale yellow	Pale yellow
CH:CBz-CN .....	Yellow or orange	Straw-yellow	Pale yellow
CH:C $\begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array}$ C <sub>6</sub> H <sub>4</sub> ...	Brick-red	Chrome-yellow	Lemon-yellow

It follows, therefore, that the salt character of a triphenylcarbinol derivative is governed by one law and its colour by another, quite independent in its operation, and, consequently, a formula for these dyes must be so adduced that it is possible to express in it how variations in colour and salt character can proceed independently. None of the formulæ proposed hitherto satisfy this condition, not even Hantzsch's "conjugation" formula (A., 1919, ii, 254). The author proceeds to develop an electrochemical hypothesis, from the two principles already laid down by him, namely, the law of the decentralisation of chemical functions (A., 1914, i, 40) and the principle of variable states (A., 1916, i, 417).

The valency of a system which is directed towards an anion is termed a "cation valency." This may have its seat in one atom of the system, but is generally divided and the partial valencies distributed over several parts of the molecule. The more the valency is subdivided, the more strongly basic will the system be. Subdivision of valencies is also the cause of colour, and auxochromes are groups which provide cationic partial valencies. In the case of the triphenylmethane compounds, any change in the cationic valency fragments of the auxochrome is accompanied by a similar change at the central carbon atom. That is, the more the auxochrome valency is subdivided the more also will the fourth valency of the central carbon atom be, and these valency fragments will be cationic, for they are opposed to the auxochrome valencies.



In the case of crystal-violet and tetramethyldiaminobenzhydrol the "formulæ of state" may be written thus:



where Aux. = auxochrome, an. = anion, and the heavy points mark the seat of cationic partial valencies. In the first compound the auxochrome and central carbon atom valencies are more scattered than in the second, and it is therefore more basic. It is not much more deeply coloured, however, from which it follows that subdivision of cationic valencies does not cause colour, and the central carbon atom in the triphenylmethane dyes is not the seat of the colour. These dyes have three seats of colour, namely, the ring carbon atoms, which are united to the central carbon atom.

The following new compounds are prepared by the condensation of the dimethoxybenzaldehydes with various agents. *ω*-Nitro-3:4-dimethoxy-*ω*-methylstyrene,  $C_6H_3(OMe)_2 \cdot CH : CMe \cdot NO_2$ , m. p. 73°, and the 2:4-dimethoxy-compound, m. p. 79°, from nitroethane under the influence of ethylamine. *β*-Nitro-3:4-dimethoxystilbene,  $C_6H_3(OMe)_2 \cdot CH : CPh \cdot NO_2$ , m. p. 109°, and the 2:4-dimethoxy-compound, m. p. 120°, from phenylnitromethane. 3:4-Dimethoxy-*α*-phenylcinnamic acid,  $C_6H_3(OMe)_2 \cdot CH : CPh \cdot CO_2H$ , m. p. 224°, and the 2:4-dimethoxy-compound, slender needles, m. p. 191°, from sodium phenylacetate and acetic anhydride. Ethyl *α*-cyano-3:4-dimethoxycinnamate,  $C_6H_3(OMe)_2 \cdot CH : C(CN) \cdot CO_2Et$ , m. p. 155°, and the 2:4-dimethoxy-compound, m. p. 143°, from ethyl cyanoacetate. *α*-Cyano-3:4-dimethoxycinnamionitrile,

$C_6H_3(OMe)_2 \cdot CH : C(CN)_2$ , m. p. 147°, and the 2:4-dimethoxy-compound, m. p. 144°, from malononitrile. Phenyl *α*-cyano-3:4-dimethoxystyryl ketone,  $C_6H_3(OMe)_2 \cdot CH : CBz \cdot CN$ , slender needles, m. p. 106°, and the 2:4-dimethoxy-compound, m. p. 156°, from *ω*-cyanoacetophenone. Phenyl *α*-cyano-3:4-methylenedioxy-styryl ketone, lemon-yellow needles, m. p. 138°, from piperonaldehyde and *ω*-cyanoacetophenone, and phenyl *α*-cyano-4-hydroxy-3-methoxystyryl ketone, deep yellow crystals, m. p. 143°, from vanillin. J. C. W.

**Resolution of Acid Salts of Dibasic Acids [into Normal Salts and Free Acids] in Aqueous Solution. IV.** TH. SABALITSCHKA (*Ber.*, 1919, 52, [B], 1776. Compare A., 1917, i, 700; 1919, ii, 282, i, 433).—Phthalic acid is not dehydrated if its ethereal solution is evaporated without a catalyst, but a trace of sulphuric acid is sufficient to cause the production of considerable quantities of the anhydride (compare Dieckmann and Hardt, A., 1919, ii, 326). After extracting a solution of normal potassium phthalate (0.54

gram in 30 c.c.) for twenty hours with ether, the extract was found to require about 1 c.c. of 0.01*N*-potassium hydroxide for neutralisation, and the aqueous solution the same amount of acid.

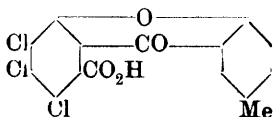
J. C. W.

**Condensation of Phthalic Anhydride with Phenols in the Presence of Aluminium Chloride.** FRITZ ULLMANN and WALTER SCHMIDT (*Ber.*, 1919, 52, [B], 2098—2118).—Phenols may be condensed with phthalic anhydride by means of aluminium chloride if acetylene tetrachloride is used as solvent, hydroxybenzoylbenzoic acid derivatives being formed in uniformly good yield. The carbonyl group of the phthalic anhydride attaches itself for the most part to the carbon atom in the *ortho*-position to the hydroxyl group of the phenol. Starting from tetrachlorophthalic anhydride, *o*-hydroxybenzoylbenzoic acid derivatives are almost exclusively obtained, which are readily converted by alkalis into xanthone derivatives.

Phthalic anhydride and *p*-cresol yield 4-hydroxy-*m*-toluoyl-*o*-benzoic acid,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , colourless, prismatic crystals, m. p. 194—195° (corr.), which is converted by sulphuric acid into 1-hydroxy-4-methylanthraquinone, reddish-yellow needles, m. p. 175° (corr.). 3-Hydroxy-*p*-toluoyl-*o*-benzoic acid, prisms, m. p. 211—212° (corr.), and 5-hydroxy-*o*-toluoyl-*o*-benzoic acid, colourless, rhombic leaflets, m. p. 219—220°, are similarly obtained from *m*-cresol, and are best separated by fractional crystallisation from nitrobenzene. In the same manner, *o*-cresol gives a mixture of 2-hydroxy-*m*-toluoyl-*o*-benzoic acid, prisms, m. p. 196—197° (corr.), and 6-hydroxy-*m*-toluoyl-*o*-benzoic acid, colourless, rhombic leaflets, m. p. 224—226° (corr.). 2'-Hydroxy-*o*-benzoylbenzoic acid, prismatic crystals, m. p. 171—172° (corr.), 4'-hydroxy-*o*-benzoylbenzoic acid, rhombic leaflets, m. p. 210° (identified by comparison with the acid obtained by the fission of phenolphthaleinoxime), and small amounts of phenolphthalein are obtained from phenol. 6-Chloro-3-hydroxy-*p*-toluoyl-*o*-benzoic acid, colourless prisms, m. p. 205—206° (corr.), is prepared from *p*-chloro-*m*-cresol, and is transformed by sulphuric acid monohydrate into 4-chloro-1-hydroxy-3-methylanthraquinone, orange-red needles, m. p. 177° (corr.). The latter is converted by *p*-toluidine in the presence of copper powder into 1-hydroxy-4-*p*-toluidino-3-methylanthraquinone, bluish-violet needles, m. p. 191° (corr.); the chlorine atom can be replaced by the hydroxyl group by treatment with sulphuric and boric acids at 150—160°, whereby 1:4-dihydroxy-2-methylanthraquinone (2-methylquinizarin), carmine-red needles, m. p. 177° (corr.), is formed. It is transformed by nitrous acid in the presence of boric and sulphuric acids into quinizarin-2-carboxylic acid, carmine-red, matted needles, m. p. 249—250° (corr.). 1-Hydroxy-4-toluenesulphonamido-3-methylanthraquinone, yellowish-brown needles, m. p. 213—214° (corr.), is obtained by heating the chlorohydroxymethylanthraquinone with potassium acetate, *p*-toluenesulphonamide, and

copper acetate in amyl-alcoholic solution, and is hydrolysed to 4-amino-1-hydroxy-3-methylantraquinone, violet needles, m. p. 257—258° (corr.). When heated with potassium and copper acetates in the presence of naphthalene, the chlorohydroxymethyl-antraquinone yields 1-hydroxy-3-methylantraquinone, m. p. 178° (corr.).

The condensation of *p*-cresol with tetrachlorophthalic anhydride gives 3:4:5:6-tetrachloro-4'-hydroxy-*m*-toluoyl-*o*-benzoic acid, m. p. 232—235° (corr.), according to the rate of heating, which is quantitatively transformed by alkali carbonate or hydroxide into 5:6:7-trichloro-2-methylxanthone-8-carboxylic acid (annexed formula), colourless, prismatic needles, m. p. 263—266° (corr.). Under

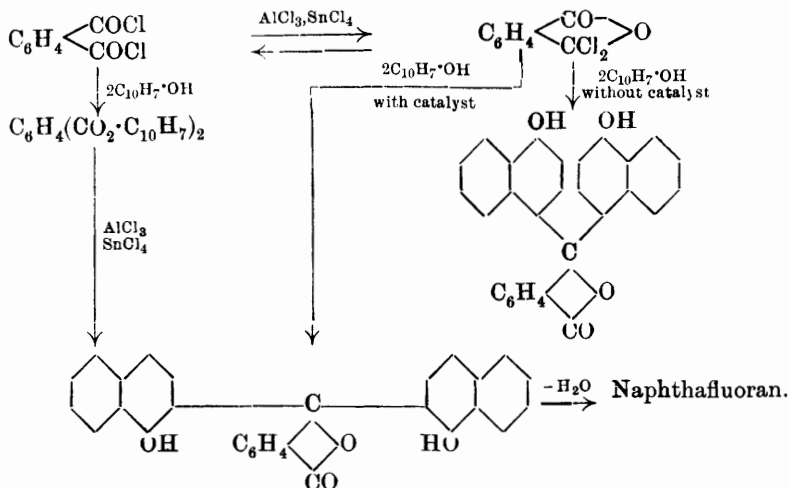


similar conditions, *m*-cresol gives 3:4:5:6-tetrachloro-3'-hydroxy-*p*-toluoyl-*o*-benzoic acid, pale yellow, prismatic plates, m. p. 226—228° (corr.), which yields 5:6:7-trichloro-3-methylxanthone-8-carboxylic acid, long, colourless, prismatic needles, m. p. 254—256° (corr., decomp.). 3:4:5:6-Tetrachloro-2'-hydroxy-*m*-toluoyl-*o*-benzoic acid, yellow, rhombic plates, m. p. 222—225° (corr.), and 5:6:7-trichloro-4-methylxanthone-8-carboxylic acid, colourless, prismatic needles, m. p. 270—273° (decomp.), are successively prepared from *o*-cresol. Phenol yields 3:4:5:6-tetrachloro-2'-hydroxy-*o*-benzoylbenzoic acid, colourless, shining leaflets, m. p. 216—218° (corr.), and 5:6:7-trichloroxanthone-8-carboxylic acid, colourless, prismatic needles, m. p. 261—264° (corr.), whilst  $\beta$ -naphthol gives 3:4:5:6-tetrachloro-2'-hydroxy-2- $\alpha$ -naphthoylbenzoic acid, yellow, rhombic plates, m. p. 214—217° (corr.), and 4':5':6'-trichloro-1:2-naphthaxanthone-1'-carboxylic acid, needles, m. p. 273—275° (corr., decomp.). H. W.

### Condensation of Phthalyl Chloride with $\alpha$ -Naphthol.

WILHELM CSÁNYI (*Ber.*, 1919, **52**, [B], 1788—1793. Compare Werner, T., 1918, **113**, 20).—The following compounds have been isolated from the product of the condensation of phthalyl chloride with  $\alpha$ -naphthol by Sørensen and Palitzsch's method (A., 1910, ii, 446). (1)  $\alpha$ -Naphthyl phthalate, pale yellow bundles of needles, m. p. 155°, insoluble in sodium hydroxide. (2) An *o*-naphtholphthalein, almost insoluble in cold alcohol, crystallising from the hot solvent in yellowish-red, prismatic needles, m. p. 234—235°; soluble with dark green colour in sodium hydroxide (compare Copisarow and Weizmann, T., 1915, **107**, 878); soluble with ultramarine colour in concentrated sulphuric acid, the solution becoming eosin-red with ochre-yellow fluorescence on warming, owing to dehydration to  $\alpha$ -naphthafuoran. (3) The *p*-naphtholphthalein, which dissolves in cold alcohol, gives a blue solution in sodium hydroxide, and cannot be condensed to the fuoran. Under the above conditions the yield of the ortho-phthalein is very small, but it is greatly increased if anhydrous aluminium or stannic chloride is present.

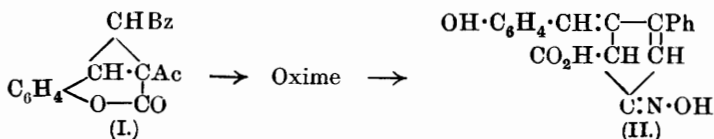
The complete system,  $\alpha$ -naphthol-phthalyl chloride, is influenced, therefore, by the tautomerism of phthalyl chloride, the equilibrium of which is displaced in favour of the unsymmetrical form by the metallic chlorides, and also by the effect of these agents on the ester (compare A., 1919, i, 327). The system is reproduced thus:



J. C. W.

**A New Group of *cyclo*Propane Derivatives. IV. Derivatives of the 3-Acyl-3:4-phenacylidenedihydrocoumarins.** OSKAR WIDMAN (*Ber.*, 1919, **52**, [B], 1652—1662. Compare A., 1918, i, 347, 398).—Some reactions of 3-acetyl- and 3-propionyl-3:4-phenacylidenedihydrocoumarins and phenacylidenecoumarinic esters are described.

3-Acetyl-3:4-phenacylidenedihydrocoumarin (I) forms an *oxime*, quadratic prisms or elongated tablets, m. p.  $230^\circ$  (decomp.), which dissolves in dilute sodium hydroxide on boiling, the yellowish-red solution depositing a *compound*, probably of the formula (II), on acidifying. This product crystallises in small, yellow tablets or prisms, m. p.  $184^\circ$  (decomp.). When treated with semicarbazide



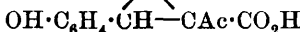
hydrochloride in methyl or ethyl alcohol, alcoholates of the semicarbazone are formed. These lose the alcohol at about  $115^\circ$  in a vacuum, giving the pale yellow *semicarbazone*,

$\text{C}_{19}\text{H}_{14}\text{O}_3\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ ,  
m. p.  $204^\circ$  (decomp.); the *compound* with  $1\text{EtOH}$ , crystallises in

long needles which change into small rhombohedra, and the compound with 1MeOH forms small, quadratic tablets. In acetic acid solution, however, the product is salicylaldehydesemicarbazone. Similarly, hydrazine hydrochloride produces the azine of salicylaldehyde.

When shaken with sodium ethoxide solution, the 3-acetyl derivative gradually deposits the yellow salt of  $\alpha$ -acetyl- $\alpha\beta$ -phenacylidene-CHBz

*dihydrocoumaric acid*, The free acid

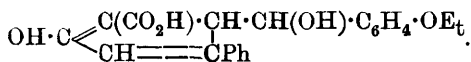


crystallises in colourless, quadratic pyramids, m. p. 177° (decomp.), and slowly reduces permanganate in acetone. The compound also dissolves in boiling 10% sodium hydroxide, depositing a scarlet, flaky salt on cooling, which evolves carbon dioxide and salicylaldehyde (?) on acidifying, thereby changing into 3-keto-1-phenyl-5-salicylidene-

$\Delta^1$ -cyclopentene,  $\text{CO} \begin{array}{c} \text{CH}_2 \cdot \text{C} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH} \\ \diagdown \quad \diagup \\ \text{CH} = \text{CPh} \end{array}$ . This crystallises in

nodules of yellow needles, m. p. 202°, readily reduces permanganate, and forms an acetyl derivative, pale yellow filaments, m. p. 161°, which yields an oxime, pale yellow filaments, m. p. 167° (decomp.), and an azine,  $[\text{C}_{20}\text{H}_{16}\text{ON}]_2\text{N}_2$ , reddish-brown filaments, m. p. 232°.

Ethyl  $\alpha$ -acetyl- $\alpha\beta$ -phenacylidenedihydrocoumarinate dissolves in dilute sodium hydroxide on boiling, and on acidifying the solution deposits 2-hydroxy-4-phenyl-5- $\alpha$ -hydroxy-o-ethoxybenzyl- $\Delta^1,^3$ -cyclopentadiene-1-carboxylic acid,

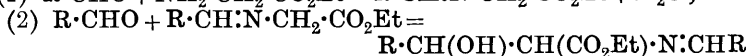
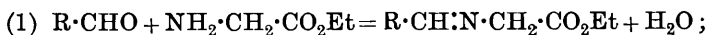


This crystallises in large, pale yellow, quadratic prisms, m. p. 164° (decomp.), gives an intense violet coloration with ferric chloride, and forms a lactone, glassy, rhombic tablets, m. p. 137—138°, on boiling with acetic anhydride.

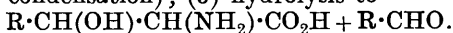
3-Propionyl-3:4-phenacylidenedihydrocoumarin reacts with dilute sodium hydroxide to form 3-keto-1-phenyl-5-salicylidene-2-methyl- $\Delta^1$ -cyclopentene, straw-yellow tablets or prisms, m. p. 250°, and ethyl  $\alpha$ -propionyl- $\alpha\beta$ -phenacylidenedihydrocoumarinate yields 2-hydroxy-4-phenyl-5- $\alpha$ -hydroxy-o-ethoxybenzyl-3-methyl- $\Delta^1,^3$ -cyclopentadiene-1-carboxylic acid, stout prisms, m. p. 138°. J. C. W.

**Hydroxy- and Dihydroxy-phenylserines and the Parent Substance of Adrenaline.** KARL W. ROSENMUND and H. DORNSAFT (*Ber.*, 1919, 52, [B], 1734—1749).—Erlenmeyer's synthesis of phenylserines from aromatic aldehydes and glycine (*A.*, 1905, i, 131) is of very limited application, but a modification which would admit of the production of phenolic serines would be of considerable interest, because of the relationship between such compounds and adrenaline. Three methods have now been tested, the third being successful, consisting in the condensation of the aldehydes

with ethyl glycine in the presence of sodium. The reaction is represented thus:

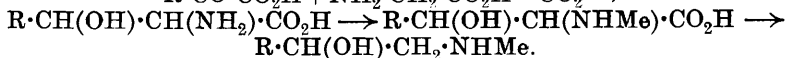
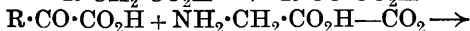
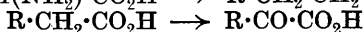
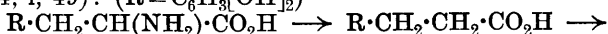


(that is, aldol condensation); (3) hydrolysis to



In the case of phenolic aldehydes, the hydroxy-groups are protected by transforming them into ethylcarbonato-groups, which are subsequently removed by treatment with dilute sodium hydroxide in an atmosphere of hydrogen (Fischer's method).

Various views on the development of adrenaline in the body are criticised, and the following scheme is suggested, the precursor being the 3:4-dihydroxyphenylalanine of proteins (Guggenheim, A., 1914, i, 49): ( $\text{R} = \text{C}_6\text{H}_3[\text{OH}]_2$ )



It is quite possible that the 3:4-dihydroxyphenylserine itself is a hydrolytic product of protein.

*The Unsuccessful Attempts.*—Anisaldehyde and ethyl chloroacetate, condensed together by Claisen's method (A., 1905, i, 286),

yield *ethyl p-methoxyphenylglycidate*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{smallmatrix} \text{O} \\ \diagup \\ \text{CH} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$

b. p. 187—191°/18 mm., and the corresponding sodium salt, which reacts with hydroxylamine hydrochloride to give the oxime of *p*-methoxyphenylacetaldehyde and carbon dioxide. Similarly, piperonaldehyde gives *ethyl 3:4-methylenedioxyphenylglycidate*, b. p. 205—210°/17 mm., and the sodium salt, which is converted into homopiperonaldoxime. These esters were expected to combine with amines to form serines, but the experiments were unsuccessful. Ethyl carbethoxyglycine,  $\text{CO}_2\text{Et} \cdot \text{NH} \cdot \text{CH} \cdot \text{CO}_2\text{Et}$ , was expected to combine with benzaldehyde in the presence of sodium to form the *N*-carbethoxy-derivative of the serine, but water is eliminated in the reaction, and the product is a mixture of an *acid* of a new type,  $\text{CHPh} \cdot \text{C}(\text{CO}_2\text{H}) \cdot \text{NH} \cdot \text{CO}_2\text{H}$ , silky leaflets, m. p. 187—190° (decomp.), and its *ethyl* ester, needles, m. p. 106—107° (decomp.).

*The Successful Experiments.*—Ethyl glycine and benzaldehyde are dissolved in ether and mixed with sodium wire. The metal is soon covered with a brown crust of the sodium salt of the phenylbenzylideneserine,  $\text{OH} \cdot \text{CHPh} \cdot \text{CH}(\text{CO}_2\text{Na}) \cdot \text{N} \cdot \text{CHPh}$ , which is removed frequently by means of a glass rod. After lifting out any unchanged metal, the sodium salt is dissolved in water and acidified with acetic acid, giving benzaldehyde and phenylserine, m. p. 192° (decomp.). Anisaldehyde behaves in the same way, yielding *p-anisylserine* [ $\alpha$ -amino- $\beta$ -hydroxy- $\beta$ -p-methoxyphenylpropionic acid], white needles, m. p. 185—186°.

*p*-Ethylcarbonatobenzaldehyde,  $\text{CO}_2\text{Et}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ , a pale yellow liquid, b. p. 170—172°/19 mm., m. p. 13°, from *p*-hydroxybenzaldehyde and ethyl chloroformate in the presence of sodium hydroxide, also reacts with glycine ester, but in this case very little sodium salt is produced. The main product is the ester of the arylbenzylideneserine, which remains in the ethereal solution and is hydrolysed and deposited as the *hydrochloride*, m. p. 181°, of the *p*-ethylcarbonatophenylserine ester, long, prismatic needles, m. p. 124°, on adding alcoholic hydrogen chloride. The free ester is obtained from the salt by means of ammonia solution, but the salt may be converted directly into *p*-hydroxyphenylserine [ $\alpha$ -amino- $\beta$ :4-dihydroxy- $\beta$ -phenylpropionic acid], small needles or leaflets, decomp. 217°, by shaking it with *N*-sodium hydroxide.

In the case of *m*-methoxy-*p*-ethylcarbonatobenzaldehyde, m. p. 71° (from vanillin), the intermediate sodium salt is deposited in small amount, the ethereal solution only being worked up, as above. *Vanillylserine* [ $\alpha$ -amino- $\beta$ :4-dihydroxy-3-methoxyphenylpropionic acid] forms slender needles, m. p. 195° (decomp.). Similarly, 3:4-diethylcarbonatobenzaldehyde, b. p. 215—217°/13 mm. (from protocatechualdehyde), yields the *hydrochloride* of 3:4-diethylcarbonatophenylserine ester,

$\text{C}_6\text{H}_3(\text{O}\cdot\text{CO}_2\text{Et})_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{NH}_2\cdot\text{HCl}$ , white druses, m. p. 151—152° (decomp.), and 3:4-dihydroxyphenylserine [ $\alpha$ -amino- $\beta$ :3:4-trihydroxyphenylpropionic acid], m. p. 208—210° (decomp.).

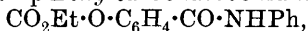
Propaldehyde does not behave at all in the same way, but gives rise to a compound of the formula  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}(\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , which crystallises in microscopic needles, decomp. 250°.

J. C. W.

**Process of Manufacturing Benzaldehyde.** A. I. APPELBAUM (U.S. Pat. 1302273).—Aldehydes are produced from aromatic hydrocarbons by heating with an oxidising agent and a catalyst in the presence of an acid. For example, a mixture of 92 parts of toluene, 100 parts of manganese dioxide, 150 parts of sulphuric acid, and 5 parts of ferric, copper, or cerium sulphate is heated to boiling in a digester, then distilled with steam, and the distillate fractionated to separate benzaldehyde from unchanged toluene.

**A New Method for the Conversion of Carboxylic Acids into Aldehydes.** ADOLF SONN and ERNST MÜLLER (*Ber.*, 1919, 52, [B], 1927—1934).—The replacement of the chlorine atom of imino-chlorides by hydrogen is readily effected by the action of stannous chloride in ethereal solution; the tin double salts of the corresponding Schiff's bases appear to be formed as intermediate products, and these pass readily into aldehydes and aniline salts when heated with dilute acids, or, in certain cases, when simply treated with steam. Thus, when a solution of benzanilideiminochloride in dry ether is gradually added to pure stannous chloride dissolved in ether in the presence of dry hydrogen chloride, the *tin* salt,  $\text{C}_{13}\text{H}_{12}\text{NCl}_3\text{Sn}$ , lemon-yellow, crystalline powder, m. p. 165° to a

foaming mass, which becomes completely liquid at  $200^{\circ}$  (decomp.), gradually separates; it is converted by dilute hydrochloric acid into benzaldehyde, the yield being practically quantitative. Similarly, cinnamaldehyde is prepared in 92% yield from cinnam-anilideiminochloride. *p*-Ethylcarbonatobenzanilide,



long, colourless needles, m. p.  $182^{\circ}$  (uncorr.), is transformed into the corresponding *iminochloride*, colourless, unstable needles, m. p.  $84^{\circ}$ , which yields *p*-hydroxybenzaldehyde, m. p.  $115\text{--}116^{\circ}$ . Similarly, 3:4:5-trimethoxybenzanilide,  $\text{C}_6\text{H}_2(\text{OMe})_3\cdot\text{CO}\cdot\text{NHPh}$ , colourless needles, m. p.  $141^{\circ}$ , gives successively the corresponding *iminochloride*, long, unstable needles, b. p.  $222\text{--}223^{\circ}/13\text{ mm.}$ , m. p.  $106^{\circ}$ , and 3:4:5-trimethoxybenzaldehyde, m. p.  $74\text{--}75^{\circ}$ .

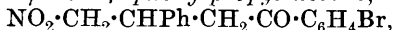
Pure stannous chloride appears to be essential for the success of the operations. Commercial grades only dissolve in ether in the presence of a large excess of hydrogen chloride, which renders the solutions unsuitable for the reduction of the more sensitive imino-chlorides.

Attempts to convert aliphatic acids into aldehydes by this process have been abortive up to the present.

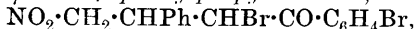
H. W.

**The cycloPropane Series. VIII. Nitrocyclopropane Derivatives.** E. P. KOHLER and H. E. WILLIAMS (*J. Amer. Chem. Soc.*, 1919, **41**, 1644—1655).—In the hope of being able to isolate some of the intermediate products which could not be examined in the earlier work (A., 1919, i, 582), the authors have turned their attention to another nitrocyclopropane derivative, and now describe *p*-bromobenzoylphenylnitrocyclopropane, which they have prepared in three of the four possible stereoisomeric forms.

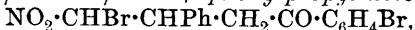
*p*-Bromophenyl  $\gamma$ -nitro- $\beta$ -phenylpropyl ketone,



small needles, m. p.  $101\text{--}102^{\circ}$  (*semicarbazone*, m. p.  $168\text{--}169^{\circ}$  [decomp.]), is prepared, together with the "dimolecular" product,  $\text{NO}_2\cdot\text{CH}(\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Br})_2$ , by the action of sodium nitromethane on  $\alpha$ -phenyl- $\gamma$ -(*p*-bromophenyl)propenone. When brominated in carbon tetrachloride solution, it yields three *p*-bromophenyl  $\alpha$ -bromo- $\gamma$ -nitro- $\beta$ -phenylpropyl ketones,



fine needles, m. p.  $114\cdot5\text{--}115\cdot5^{\circ}$ , rhombic tables, m. p.  $105\text{--}106^{\circ}$ , and needles, m. p.  $91^{\circ}$ , respectively, and a dibromo-compound, thin flakes, m. p.  $138\text{--}139^{\circ}$ . Bromination in the  $\alpha$ -position to the nitro-group is effected by means of the sodium derivative, whereby *p*-bromophenyl  $\gamma$ -bromo- $\gamma$ -nitro- $\beta$ -phenylpropyl ketone,

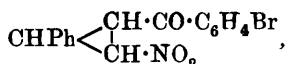


is obtained in needles, m. p.  $127^{\circ}$ , whilst the corresponding  $\gamma\gamma$ -dibromo-product forms thin plates or needles, m. p. about  $144\text{--}146^{\circ}$ . Since it has been previously shown that it is possible to distinguish between bromine compounds in which the bromine is in the  $\alpha$ -position to the nitro-group and those in which it is in the  $\alpha$ -position relative to the carbonyl by treatment with potassium



iodide, the former undergoing reduction, whilst the latter are transformed into the corresponding iodo-derivatives, the foregoing bromo-derivatives have been boiled with potassium iodide in alcoholic solution; the reaction is found to be a general one, and the following substances are obtained: *p*-bromophenyl  $\alpha$ -iodo- $\gamma$ -nitro- $\beta$ -phenylpropyl ketone, pale yellow, rhombic plates, m. p.  $110^\circ$ , from the isomerides, m. p.  $114.5$ — $115.5^\circ$  and  $105$ — $106^\circ$  respectively; the nitro-ketone from the  $\gamma$ -monobromo-derivative, and first the  $\gamma$ -monobromo-compound, m. p.  $127^\circ$ , and then the nitro-ketone from the  $\gamma\gamma$ -dibromo-derivative.

3-Nitro-2-*p*-bromobenzoyl-1-phenylcyclopropane,

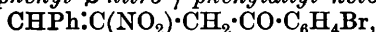


m. p.  $131^\circ$ , is obtained by the action of fused potassium acetate on an alcoholic solution of the  $\alpha$ -bromo-compound; similar treatment of the  $\gamma$ -bromo-compound leads to the formation of an isomeric cyclopropane derivative, fine needles, m. p.  $115^\circ$ , possibly formed as a result of prolonged contact with potassium acetate, since the same substance is formed from the isomeride, m. p.  $130^\circ$ , under similar conditions. A third isomeride, needles, m. p.  $162$ — $163^\circ$ , is formed when an alcoholic suspension of either of the other two is treated with very dilute sodium methoxide solution. All three substances give the corresponding open-chain, saturated nitro-ketone, colourless needles, m. p.  $101^\circ$ , when reduced with zinc dust and alcohol. The substance, m. p.  $130^\circ$ , readily combines with hydrochloric acid, giving *p*-bromophenyl  $\gamma$ -chloro- $\beta$ -nitro- $\gamma$ -phenylpropyl ketone,  $\text{CHPhCl} \cdot \text{CH}(\text{NO}_2) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Br}$ , long, slender needles, m. p.  $133^\circ$ , which on treatment with potassium acetate loses nitrous acid, yielding a mixture of stereoisomeric *p*-bromophenyl  $\gamma$ -chloro- $\gamma$ -phenyllallyl ketones, downy needles, m. p.  $179$ — $180^\circ$ , and yellow plates, m. p.  $108$ — $109^\circ$ , the constitution of which is deduced from the fact that either is converted by permanganate into benzoic and *p*-bromobenzoic acids, and by ozone into *p*-bromobenzoic acid and benzoyl chloride. The hydrochloric acid additive product readily loses hydrogen chloride and nitrous acid when boiled in alcoholic solution, and yields 2-phenyl-5-*p*-bromophenylfuran,



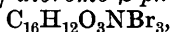
colourless or very pale yellow flakes, m. p.  $127^\circ$ . The cyclopropane derivatives, m. p.'s  $130^\circ$  and  $162^\circ$  respectively, readily unite with hydrogen bromide, and, according to the manner in which the experiment is conducted, yield two substances,  $\text{C}_{16}\text{H}_{13}\text{O}_3\text{NBr}_2$ , colourless needles, m. p.  $144^\circ$  (decomp.), and long needles, m. p.  $133^\circ$ , which are similarly constituted to the hydrogen chloride additive compound, since, like this, they readily pass into the same 2-phenyl-5-*p*-bromophenylfuran. On the other hand, they lose halogen acid more easily than nitrous acid when treated with potassium acetate,

yielding *p*-bromophenyl  $\beta$ -nitro- $\gamma$ -phenylallyl ketone,



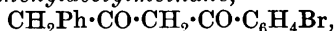
unstable colourless needles, m. p. 162—163° (decomp.).

The cyclopropane derivatives react slowly with bromine when dissolved in boiling carbon tetrachloride and placed in direct sunlight. In this manner, the isomeride, m. p. 130°, yields two isomeric *p*-bromophenyl  $\alpha$ -dibromo- $\beta$ -phenylpropyl ketones,



m. p.'s 162—163° and 137° respectively, which can also be prepared by the action of bromine on the  $\gamma$ -bromo-additive product of hydrogen bromide and the cyclopropane derivative. (A third substance,  $\text{C}_{16}\text{H}_{12}\text{OBr}_4$ , fine crystalline powder, m. p. 190—193°, which is probably a furan derivative, is also obtained.) When treated with potassium iodide, the bromine additive compounds yield *p*-bromophenyl  $\beta$ -nitro- $\gamma$ -phenylpropenyl ketone, yellow plates, m. p. 115°, the constitution of which follows from its oxidation to *p*-bromobenzoic and phenylacetic acids.

The action of dilute sodium methoxide solution in converting the cyclopropane derivatives of lower m. p. into the isomeride of highest m. p. is somewhat difficult to interpret, but by cautious regulation of the reaction it has been found possible to isolate the methoxy-compound,  $\text{CH}_2\text{Ph} \cdot \text{C}(\text{OMe}) \cdot \text{CH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Br}$ , thin needles, m. p. 102—103°, which is a possible intermediate product; the composition of the substance is deduced from its oxidation by permanganate in acetone solution to methyl phenylacetate and *p*-bromobenzoic acid. It is easily hydrolysed by hydrochloric acid to *p*-bromobenzoylphenylacetyl methane,



rhombic plates, m. p. 80—81°, which readily gives a pale green copper derivative.

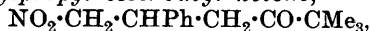
H. W.

**The cycloPropane Series. IX. Nitrocyclopropane Derivatives.** ELMER PETER KOHLER and M. SRINIVASA RAO (*J. Amer. Chem. Soc.*, 1919, 41, 1697—1704).—The nitrocyclopropane derivatives described previously have all contained an aryl group; the authors now describe a similar compound with an alkyl group, and, in order to avoid complications in the preparation, have used *tert*-valeryl compounds, the substance studied being 3-nitro-2-*tert*-

butyryl-1-phenylcyclopropane,  $\text{CHPh} \begin{matrix} \text{CH} \cdot \text{NO}_2 \\ \text{CH} \cdot \text{CO} \cdot \text{CMe}_3 \end{matrix}$  which is pre-

pared by the usual methods. The substitution of the *tert*-butyl- for the phenyl-group does not materially affect the properties of the cyclopropane derivative, and, unfortunately, does not lower the boiling points of the substances sufficiently to make distillation under reduced pressure feasible. The new cyclopropane readily combines with other substances, and the ring opens in all cases between the carbon atoms attached to the phenyl and trimethylacetyl groups.

$\gamma$ -Nitro- $\beta$ -phenylpropyl *tert*-butyl ketone,



minute, colourless plates, m. p. 74°, is prepared by the action of sodium

methoxide on benzyldenepinacoline and nitromethane. When brominated in carbon tetrachloride solution it yields two isomeric  $\alpha$ -bromo- $\gamma$ -nitro- $\beta$ -phenylpropyl tert.-butyl ketones, large needles, m. p. 143—144°, and colourless plates, m. p. 74—75°, the latter of which is readily transformed into the former by boiling with methylalcoholic potassium acetate. Both isomerides are slowly converted into 3-nitro-2-tert.-valeryl-1-phenylcyclopropane, cubes, m. p. 94°, by the regulated action of potassium acetate in boiling methylalcoholic solution. This substance readily loses nitrous acid under the influence of alkalis, and yields phenylacetyl-tert.-valeryl-methane,  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CMe}_3$ , needles, m. p. 44°, which has also been directly synthesised from ethyl phenylacetate and pinacoline. With phenylcarbimide it yields a phenylcarbamate, m. p. 130—132°, and with hydroxylamine it gives 5-benzyl-3-tert.-butylisooxazole, m. p. 51°, and 3-benzyl-5-tert.-butylisooxazole, m. p. 63°. The nitrocyclopropane combines very readily with hydrogen bromide to form  $\gamma$ -bromo- $\beta$ -nitro- $\gamma$ -phenylpropyl tert.-butyl ketone,  $\text{CHPhBr}\cdot\text{CH}(\text{NO}_2)\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CMe}_3$ , very unstable crystals, m. p. 66—67°, which readily lose both nitrous acid and hydrogen bromide; with cold potassium acetate, however, chiefly the latter is eliminated with production of  $\beta$ -nitro- $\beta$ -benzyldene-ethyl tert.-butyl ketone,  $\text{CHPh}\cdot\text{C}(\text{NO}_2)\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CMe}_3$ , long, yellow unstable needles, m. p. 53—54°, in which the double bond must be adjacent to the phenyl group, since benzaldehyde is formed as primary product of its oxidation by permanganate in acetone solution. When the unsaturated nitro-ketone is treated with hydrogen bromide in glacial acetic acid solution, it not only unites with the acid, but also undergoes reduction, yielding 5-bromobenzyl-3-tert.-butylisooxazole, needles, m. p. 77—78°, which is reduced by zinc dust and acetic acid to 5-benzyl-3-tert.-butylisooxazole, m. p. 50°.

H. W.

**Pyrylium Compounds. V. Enolic and Ketonic Forms of Unsaturated 1:5-Diketones.** W. DILTHEY and TH. BÖTTLER (*Ber.*, 1919, **52**, [B], 2040—2054).—The conversion of the condensation product of phenyl styryl ketone and deoxybenzoin into a pyrylium salt has been previously described (*A.*, 1917, i, 578). The pseudo-base corresponding with the latter has now been investigated and is shown to be  $\alpha$ -hydroxy- $\epsilon$ -keto- $\alpha\gamma\delta\epsilon$ -tetraphenyl- $\Delta^{\alpha\gamma}$ -pentadiene,  $\text{OH}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{COPh}$ ; when treated with a moderate amount of alkali, it readily passes into the corresponding diketones. The first case of keto-enolic desmotropy in unsaturated 1:5-diketones is thus presented.

2:3:4:6-Tetraphenylpyryl ferrichloride,  $\text{C}_{20}\text{H}_{21}\text{OCl}_4\text{Fe}$ , yellow, shining prisms, m. p. 186°, is prepared by adding hydrated ferric chloride to a warm solution of  $\alpha\epsilon$ -diketo- $\alpha\gamma\delta\epsilon$ -tetraphenylpentane in acetic acid and acetic anhydride. When warmed with water in the presence of ether, it gives  $\alpha$ -hydroxy- $\epsilon$ -keto- $\alpha\gamma\delta\epsilon$ -tetraphenyl- $\Delta^{\alpha\gamma}$ -pentadiene, pale yellow needles, united in clusters, m. p. 112—113°, from which the iron salt is readily re-formed. It does

not dissolve in aqueous alkalis, but forms deep violet solutions with alcoholic alkalis. It is rapidly transformed by alcoholic ammonia into 2:3:4:6-tetraphenylpyridine, m. p. 182°. It is rapidly oxidised by permanganate in pyridine solution, yielding benzoic acid, benzoylformic acid, and benzil. Acetylation with acetic anhydride and sodium acetate leads to the formation of *αε-diketo-β-acetyl-αγδε-tetraphenyl-Δγ-pentene*,  $\text{COPh}\cdot\text{CHAc}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{COPh}$ , needles, m. p. 172—173°, which gives the ketone, m. p. 142° (*v.c.*), when hydrolysed with alcoholic potassium hydroxide. Attempts to obtain benzoyl- or alkyl-derivatives were unsuccessful. Semicarbazide yields a *mono-semicarbazone*, short, colourless prisms, m. p. 225—226° (decomp.). The enol reacts but slowly with bromine at the ordinary temperature, but, at 30°, the latter is decolourised, and a *substance*, pale yellowish-green prisms, m. p. 166—167°, is formed to which the constitution  $\text{PhC} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{C}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{COPh}$ , is

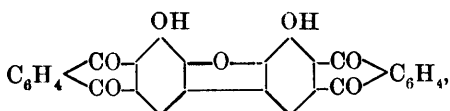
ascribed. The following salts of the *pseudo-base* are described: *platinichloride*,  $\text{C}_{58}\text{H}_{45}\text{O}_2\text{Cl}_4\text{Pt}$ , orange-yellow leaflets, m. p. 229—230°; *zincchloride*, lemon-yellow leaflets, m. p. 295—296°; *stannichloride*, yellow needles, m. p. 134—135°; *perchlorate*, canary-yellow, shining needles, m. p. 261°; *periodide*,  $\text{C}_{29}\text{H}_{21}\text{OI}_3$ , brownish needles, m. p. 218°; *perbromide*, short, yellow needles, m. p. 217° (also obtained but with greater difficulty from the isomeride, m. p. 142°); *hydrogen bromide*, yellow prisms which when rapidly heated eliminate hydrogen bromide at about 150° and finally melt at 233—235°; *normal bromide*, coarse, orange-red prisms, m. p. 237—238°.

The enolic form is quantitatively converted into *αε-diketo-αγδε-tetraphenyl-Δγ-pentene*,  $\text{COPh}\cdot\text{CH}_2\cdot\text{CPh}\cdot\text{CPh}\cdot\text{COPh}$ , when its solution of methyl alcohol is gently warmed with a solution of sodium (1 atom) in the same solvent; it forms colourless, shining needles, m. p. 142—143°, and is less soluble than the enol in all solvents. It is much more stable than the enolic form both towards permanganate and towards bromine; with the latter, however, it slowly yields the same substance, m. p. 166°, which is obtained from the enol. It slowly yields the pyrylium salts which are instantly formed from the enolic variety. Acetylation converts it into the same acetyl derivative as is obtained from the enol. Semicarbazide slowly yields the *α-semicarbazone* of *αε-diketo-αγδε-tetraphenyl-Δγ-pentene* (see above). [A similar slow reaction is observed with the corresponding saturated diketone, whereby the *α-semicarbazone* of *αε-diketo-αγδε-tetraphenylpentane*, m. p. 238—239°, is produced.] The ketonic is converted into the enolic form by the action of an excess of alcoholic potassium hydroxide. H. W.

**Preparation of Benzoquinone.** JOHN M. WEISS and CHARLES R. DOWNS (U.S. Pat. 1318631).—Benzoquinone is produced by subjecting benzene in the vapour phase to the action of a gas containing oxygen at a suitable temperature and in the presence of a catalyst. G. F. M.

**Reduction of Dihydroxythymoquinone by means of Palladium Hydrogen.** NELLIE A. WAKEMAN (*J. Amer. Chem. Soc.*, 1919, **41**, 1873—1875).—Thymoquinone is very readily reduced by hydrogen in alcoholic solution in the presence of palladium chloride with the formation of hydrothymoquinone. Similar attempts to reduce dihydroxythymoquinone in alcoholic or ethereal solution were only partly successful, since, although reduction occurred very readily and the solutions became decolorised, the product reverted so easily to the red dihydroxythymoquinone that its isolation in the pure condition was impossible. By performing the experiment in acetic anhydride solution, however, it was found that reduction occurs with less rapidity, but gives an almost quantitative yield of the desired *tetra-acetyl* derivative, colourless, prismatic crystals, m. p. 180—182°, which is stable in air and, on hydrolysis, yields dihydroxythymoquinone in practically quantitative amount. The palladium chloride appears to suffer no loss of activating power when used repeatedly in these experiments. H. W.

**Action of Potassium Hypochlorite on Alizarin in Alkaline Solution.** R. SCHOLL [with ÉMIL SCHWINGER and ALB. KABATSCNIK] (*Ber.*, 1919, **52**, [B], 1829—1836. Compare A., 1919, i, 25, 406).—Whereas alkaline ferricyanide solutions cause rupture of the hydroxylated ring of alizarin, the oxidative activity of hypochlorites is manifested in the production of dianthraquinonyl derivatives. The oxidation may be performed by adding potassium hypochlorite solution to a solution of alizarin in potassium hydroxide, or by dissolving the substance in 8% potassium hydroxide and passing in chlorine. The chief product separates as a bluish-black *potassium* salt which is decomposed by dilute sulphuric acid and the acid purified by boiling with nitrobenzene. The product, 3:4:3':4'-*tetrahydroxy-2:2'-dianthraquinonyl*,  $C_{28}H_{14}O_8$ , forms dark yellowish-red, microscopic, rhombic or hexagonal, prismatic tablets, m. p. 384—395°, and its *sodium* salt is dark blue. It has no affinity for un-mordanted fibres, and is much poorer as a mordant dye than alizarin. The *tetra-acetate* forms yellow crystals, m. p. 278—280°. When distilled with zinc dust in an atmosphere of hydrogen, under 15—30 mm. pressure, it yields 2:2'-*dianthrlyl*,  $C_{28}H_{18}$ , yellow, rhombic leaflets, with green fluorescence, m. p. 355°, which is also formed when 2:2'-dianthraquinonyl (A., 1911, i, 453) is treated in the same way. 1:1'-Dianthraquinonyl, however, does not yield the unknown 1:1'-dianthrlyl under these conditions, but rather *meso-naphthadanthrone* (A., 1910, i, 494). When heated with zinc chloride, the tetrahydroxydianthraquinonyl gives 4:4'-*dihydroxy-2:2'-dianthraquinylene-3:3'-oxide*,



which crystallises in yellow needles, m. p. 390—400° (decomp.).

J. C. W.

**Synthesis of some Homologues of the Terpenes: Derivatives of 1:4-Diisopropylcyclohexane.** MARSTON TAYLOR BOGERT and CLARENCE PEAVY HARRIS (*J. Amer. Chem. Soc.*, 1919, **41**, 1676—1690).—The peculiar properties of the terpenes appear to be generally associated with the presence of an isopropyl and a methyl group, and seem to be due to the former rather than the latter; whilst numerous derivatives having one such group have been investigated, little is known of the effect of two of these groups. The authors have therefore investigated a series of homologues of *p*-diisopropylbenzene, which are prepared by the action of magnesium methyl iodide on the methyl ester of terephthalic and partially hydrogenated terephthalic acids and subsequent elimination of water if necessary.

*p*-Dihydroxyisopropylbenzene,  $C_6H_4(CME_2 \cdot OH)_2$ , colourless, short, lustreless needles, m. p.  $142.4-142.9^\circ$  (corr.), is obtained from magnesium methyl iodide and methyl terephthalate (the method of achieving the regulated addition of the reagent to the ester, which is only sparingly soluble in ether, is fully described in the original); when distilled with potassium hydrogen sulphate under diminished pressure, it yields 1:4-diisopropenylbenzene, micaceous plates, m. p.  $63.6-64^\circ$  (corr.), which readily unites with four atoms of bromine without evolution of hydrogen bromide (the tetrabromide could not be isolated in the pure condition). Similarly, methyl  $\Delta^{1,4}$ -dihydroterephthalate, m. p.  $128.4-129.4^\circ$  (corr.), yields 1:4-diisopropenyl- $\Delta^{1,4}$ -cyclohexadiene, plates, m. p.  $117-117.5^\circ$  (corr.), the dicarbinol formed as an intermediate product eliminating water spontaneously. The substance adds four atoms of bromine, but hydrogen bromide is readily evolved; however, by suitable adjustment of conditions, a small quantity of the tetrabromide, cubic crystals, m. p.  $107-109^\circ$  (corr.), was isolated.

The main product of the action of the Grignard reagent on methyl  $\Delta^1$ -tetrahydroterephthalate, b. p.  $153.3-154.5^\circ$  (corr.)/20 mm., m. p.  $35.2-36.2^\circ$  (corr.), appears to be the corresponding dicarbinol which, however, could not be isolated in the pure condition. The crude product was therefore dehydrated with potassium hydrogen sulphate, whereby two isomeric hydrocarbons,  $C_{12}H_{18}$ , b. p.'s  $95-98^\circ/20$  mm. and  $105-108^\circ/20$  mm. respectively, were produced. Both are colourless oils, which become viscous and slightly yellow on prolonged exposure to air. Both absorb bromine quickly at the outset, but evolution of hydrogen bromide soon begins, so that no pure bromine derivatives could be separated.

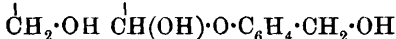
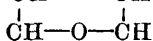
The densities, refractive indices, and magnetic rotatory powers of the new hydrocarbons in the pure state and in a number of solvents have been determined, and the data are discussed with reference to their bearing on the structures assigned to these compounds.

H. W.

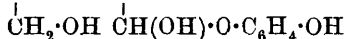
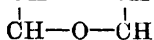
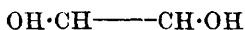
**Constituents of Resins. Degradation of *d*-Sumaresinolic Acid.** ALOIS ZINKE (*Monatsh.*, 1919, **40**, 277—280).—When *d*-sumaresinolic acid is oxidised by chromic acid in glacial acetic acid solution, a monocarboxylic acid,  $C_{27}H_{40}O_4$ , is obtained, which is

isomeric with the acid obtained from *d*-siaresinolic acid (A., 1919, i, 129); it is best purified by crystallisation from benzene, from which it separates in coarse prisms + C<sub>6</sub>H<sub>6</sub>, the solvent being only completely expelled at 150° in a vacuum. The pure substance has m. p. 260—261°. The *barium* salt is described. When thus oxidised, *d*-sumaresinolic acid loses three carbon and eight hydrogen atoms; hence it probably contains a propyl or *isopropyl* group, and its formula may be written C<sub>26</sub>H<sub>40</sub>O<sub>2</sub>(C<sub>3</sub>H<sub>7</sub>)·CO<sub>2</sub>H. H. W.

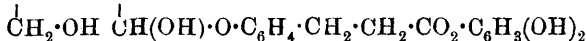
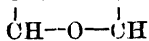
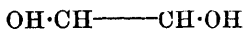
**The Distillation of certain Glucosides under Reduced Pressure.** AMÉ PICTET and HENRY GOUDET (*Helv. Chim. Acta*, 1919, 2, 698—703).—The fact that the majority of the naturally occurring glucosides are lævrotatory, although yielding dextrose on hydrolysis, has led the authors to doubt whether they are in reality derivatives of the latter substance. To throw light on the question, they have distilled salicin, arbutin, and phloridzin under reduced pressure, and, in each case, have isolated lævoglucozan (compare Tanret, A., 1894, i, 564; Pictet and Sarasin, A., 1918, i, 59) from among the products of distillation. They are therefore led to suggest the annexed formulæ for the glucosides:



Salicin.

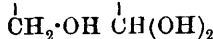
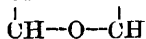
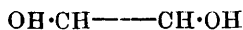


Arbutin.



Phloridzin.

Hydrolysis of the glucosides by barium hydroxide solution yields primarily an unstable hydrate (annexed formula), which passes into lævoglucozan by loss of water. With acids, the rupture of the ring also occurs with formation of dextrose.



Salicin, on distillation, yielded an aqueous liquid containing a little furfuraldehyde, and a pasty mass from which lævoglucozan, m. p. 179—180°,  $[\alpha]_D^{20} - 66.73^\circ$  in aqueous solution, was isolated. Arbutin gave an aqueous liquid containing acetic acid and furfuraldehyde, and a pasty mass from which lævoglucozan and quinol were obtained, whilst phloreitic acid, phloroglucinol, and lævoglucozan were isolated from the semi-solid product from phloridzin. H. W.

**Chemistry and Pharmacology of Aloes. I. Products of the Oxidation of the Constituents of Aloes by means of Alkali Persulphate.** EUGEN SEEL (*Arch. Pharm.*, 1919, 257, 212—228. Compare A., 1901, i, 92; 1917, i, 41, 577).—The constituents of aloes of pharmacological importance are: (1) Aloin, which is crystalline and soluble in water; (2) aloëtin, which is amorphous and soluble in water; (3) resin or crude resin, which is amorphous and insoluble in water in the cold; (4) emodin, which occurs to the extent of less than 1%, and is very sparingly soluble even in hot water. The products obtained when the first three of these components are oxidised with potassium or ammonium persulphate have been studied.

In the case of aloin, the oxidation proceeds most simply and smoothly in very dilute aqueous solution, a series of colour changes taking place. According as the reaction is slow or rapid, it yields puraloin I either alone or mixed with puraloin II. These two products form red or brownish-red, amorphous powders, and have not been obtained quite free from ash. The results of analyses and molecular weight determinations of their derivatives indicate the formulæ,  $C_{12}H_{10}O_6$  for puraloin I, and  $C_{13}H_{12}O_6$  for puraloin II. Both are partly hydrated, and they dissolve in alkalis or concentrated acids, giving faintly violet-red or reddish-brown colorations; they are not resolved by acids, but are converted to a greater or less extent into a black powder, termed puralonigrin, owing to its analogy to alonigrin. The formulæ indicate the absence from the puraloins of an anthraquinone nucleus, and puraloin I is regarded as a dihydroxymethyldihydronaphthaquinonecarboxylic acid, and puraloin II as a dihydroxymethyldihydronaphthaquinone-acetic acid. Quantitative study of the oxidation of aloin by persulphate indicates that the sugar-residue of the glucoside is oxidised to carbon dioxide, and that part of the anthraquinone ring also undergoes attack. Since the oxidation products are insoluble in water and dilute acid, and are thus precipitated and protected from further oxidation, the reaction lends itself to the quantitative evaluation of aloes.

Oxidation of aloin by persulphate in alkaline solution yields products which are more untractable than the puraloins, and have not been investigated in detail.

*Puraloin I*, which is insoluble in 96% alcohol, blackens at 230—240°, and sinters and decomposes at about 340—350°. *Puraloin II* differs from puraloin I principally in its solubility in 96% alcohol. Both are capable of acetylation, the products being non-crystalline and possessed of a marked tendency to form colloidal solutions. *Triacetyl-puraloin I*,  $C_{12}H_7O_6Ac_3$ , is yellowish-brown, and sinters and turns brown at 180—190°. *Diacetyl-puraloin II* (?),  $C_{13}H_{10}O_6Ac_2$ , is brown, and remains unchanged at 300°. On benzylation, puraloin I yields a reddish-yellow powder which is intermediate in composition between the di- and tri-benzoyl derivatives, and gradually decomposes and blackens at above 200°. *Dibenzoyl-puraloin II*,  $C_{13}H_{10}O_6Bz_2$ , forms a reddish-yellow



powder, and sinters at  $220^{\circ}$  and carbonises at a higher temperature. Both puraloinis yield ochre-yellow *monobromo*-derivatives,  $C_{12}H_9O_6Br$  and  $C_{13}H_{11}O_6Br$  respectively, which gradually darken at above  $200^{\circ}$ .

The action of persulphate on aloëtin yields principally puraloinis I and II, but the proportions of secondary products are greater than those obtained from aloin. Oxidation of the crude resin also yields the two puraloinis.

When administered in single doses of 0.5—2.0 grams, the puraloinis exert a mild laxative action, which occasionally fails, but is most trustworthy with children and dogs.

T. H. P.

### Chemistry and Pharmacology of Aloes. II. Products of the Oxidation of the Constituents of Aloes by Caro's Acid.

EUGEN SEEL (*Arch. Pharm.*, 1919, **257**, 229—254. Compare A., 1901, i, 92; 1917, i, 577, and preceding abstract).—Of the products obtained by oxidising aloin by means of Caro's acid, the following have been identified: (1) A small proportion of trihydroxymethyl-anthraquinone, m. p.  $223-224^{\circ}$ , already known. (2) Two isomeric tetrahydroxymethylanthraquinones, m. p.  $185-190^{\circ}$  and  $232-234^{\circ}$  respectively, not previously described in the literature. (3) Numerous hydrogenated tri- and tetra-hydroxymethylanthraquinones, which form products intermediate to aloin and the anthraquinone derivatives, but are not obtained in sufficient quantities to admit of isolation. (4) Three naphthalene derivatives, the compositions of which have not been determined. (5) A compound which was isolated in the form of its bromo-derivative, and may be a derivative of either anthracene or naphthalene.

*Tetrahydroxymethylanthraquinone*,  $C_{15}H_{10}O_5$ , forms red crystals, m. p.  $185-190^{\circ}$ , and its *isomeride*, red crystals, m. p.  $232-234^{\circ}$ . Acetylation of these compounds yields mostly tarry masses, from which only a small proportion of *tetra-acetyl* derivative,  $C_{15}H_6O_6Ac_4$ , is obtainable as a bright yellow, crystalline powder, m. p.  $196-198^{\circ}$ ; this acetyl derivative dissolves in concentrated sulphuric acid to a violet solution, and on hydrolysis yields the tetrahydroxymethylanthraquinone, m. p.  $232-234^{\circ}$ . Benzoylation of the two compounds gives (1) a tetrabenzoyl derivative,  $C_{15}H_6O_6Bz_4$ , which forms a pale ochre-yellow, microcrystalline powder, m. p.  $236-238^{\circ}$ , dissolves in concentrated sulphuric acid to a violet-red solution, and on hydrolysis yields the tetrahydroxymethylanthraquinone, m. p.  $232-234^{\circ}$ ; (2) a *compound*, m. p.  $225-226^{\circ}$ , which differs appreciably in composition from the tetrabenzoyl derivative, and on hydrolysis gives only the tetrahydroxymethylanthraquinone, m. p.  $232-234^{\circ}$ , although it is obtained from the isomeride with m. p.  $185-190^{\circ}$ . Whether the latter is isomeric with the compound, m. p.  $232-234^{\circ}$ , or merely an impure form of it, is still uncertain.

After complete extraction of the oxidation products of aloin with chloroform or ether, extraction with 90—96% alcohol removes a compound which blackens slowly at above  $240^{\circ}$  and agrees approximately in composition with puraloin I, although in solu-

bility in strong alcohol it corresponds with puraloin II. This compound yields an *acetyl* derivative,  $C_{12}H_5O_6Ac_3$  or  $C_{12}H_7O_6Ac_3$ , which forms yellowish-white flocks, m. p. 115—120°, and a *tribenzoyl* derivative,  $C_{12}H_5O_6Bz_3$  or  $C_{12}H_7O_6Bz_3$ , which sinters at 220° and melts and decomposes at 240°. A compound of similar composition to that soluble in strong alcohol may afterwards be extracted from the oxidation products by means of dilute alcohol.

The action of Caro's acid on aloëtin yields: (1) Trihydroxymethylantraquinone, m. p. 223—224°. (2) A tetrahydroxymethylantraquinone agreeing in properties with the compound, m. p. 232—234°, but having m. p. 215°. (3) A compound,  $C_{13}H_{10}O_6$ , which has no sharp melting point, and yields a diacetyl derivative, apparently with simultaneous loss of water, and a dibenzoyl derivative,  $C_{13}H_8O_6Bz_2$ , showing incipient fusion at 225° and carbonisation at a higher temperature. (4) A small proportion of a dark brown powder which does not melt sharply, but blackens at a high temperature, and has approximately the composition of puraloin I. (5) A compound separable as its bromo-derivative, which darkens at 180°, but does not melt at 290°, and has the properties, but not the composition, of the bromo-derivative similarly obtained from the oxidation products of aloin.

The products obtained when the resin is oxidised by means of Caro's acid indicate that this resin consists mostly of resinified aloëtin, together with a little resinified aloin.

Oxidation of emodin by Caro's acid yielded no well-defined products, but the results obtained show that emodin is not readily converted into a tetrahydroxymethylantraquinone in this way.

Trihydroxymethylantraquinone or emodin acts as a mild purgative, without secondary effects, when administered to man and animals in doses of 0.2—0.4 gram at intervals of three hours, whereas smaller doses often produce such secondary effects and are sometimes without purgative action. Tetrahydroxymethylantraquinone or hydroxyemodin has a weaker purgative effect than emodin, doses of 0.5 gram being often necessary; like emodin, it may be administered subcutaneously.

T. H. P.

**Chemistry and Pharmacology of Aloes. III. Products of the Oxidation of the Constituents of Aloes by Hydrate of Sodium Peroxide.** EUGEN SEEL (*Arch. Pharm.*, 1919, 257, 254—259).—Oxidation of aloin by means of sodium peroxide yields emodin and a residue which, when treated with bromine, gives a crystalline *dibromo*-derivative, darkening at about 145°, m. p. 160—162° (decomp.), corresponding in composition with a dibromide of puraloin I,  $C_{12}H_8O_6Br_2$ . Thus, by sodium peroxide in alkaline solution, aloin is only partly resolved into emodin, the greater part of the molecule, including the sugar residue, being attacked only by persulphate. These results confirm the glucosidic character of aloin (compare Léger, A., 1904, i, 907).

The action of sodium peroxide on aloëtin is similar to that on aloin, the yield of emodin being very small; with the crude resin,

also, only small proportions of emodin are obtained. Emodin itself is not oxidised further by sodium peroxide, but may be partly purified, only the anthraquinone derivative remaining unaltered.

T. H. P.

**Anemonin. III. Constitution of Anemolic Acid.** Y. ASAHINA and A. FUJITA (*Yakugaku Zasshi* [*J. Pharm. Soc. Japan*], 1919, **448**, 471—484).—Anemonin suspended in methyl alcohol and reduced with 3% sodium amalgam and glacial acetic acid at 5° gave *dihydroanemonin*,  $C_{10}H_{10}O_4$ , m. p. 172°, in 80—90% yield, which exhibits a normal molecular weight in freezing phenol. It is easily transformed by heating with hydrochloric acid into *anemolic acid*,  $C_{10}H_{14}O_6$ , which yields a *disemicarbazone*,  $C_{12}H_{20}O_8N_8$ , m. p. 158°. When the acid is dissolved in ammonia, it gives a precipitate,  $C_{10}H_{16}O_4N_2$ , which has m. p. 195° after recrystallisation from hot water, gives the pine-shaving reaction, and with hydrochloric acid yields pyrrole-2:5-dipropionic acid, m. p. 170°. From these facts, the authors conclude that anemolic acid is identical with dilævulinic acid, a conclusion confirmed by comparison with the substances synthesised by Kehrer and Hofacker's method (A., 1897, i, 214). On the other hand, sebacic acid, m. p. 131°, is obtained when dihydroanemonin is reduced with platinum black and hydrogen. So far as is known, dihydroanemonin ought to have a constitution similar to that of angelicolactone. Dihydroanemonin when boiled with anisaldehyde and aniline yields a light yellow condensation product,  $C_{26}H_{22}O_6$ , m. p. 200°.

CHEMICAL ABSTRACTS.

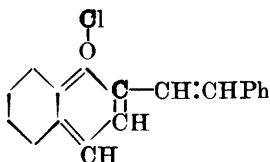
**The Tinctorial Properties of some Anthocyanins and certain Related Compounds. I.** ARTHUR E. EVEREST and ARCHIBALD J. HALL (*J. Soc. Dyers*, 1919, **35**, 275—279).—The authors record dyeing tests of various anthocyanins and anthocyanidins, and of the colouring matters of the viola, rose, lupin, pelargonium, sweet pea, bilberry, black currant, cranberry, and radish.

An improved process is given for the preparation of 2-*o*-hydroxystyrylbenzopyrylium chloride, which the authors find to have the formula  $C_{17}H_{13}O_2Cl \cdot 2H_2O$  (compare Decker and Felser, A., 1908, i, 906, who give  $1H_2O$ ).

When salicylaldehyde is condensed with styryl methyl ketone. yellow crystals of a substance, possibly of the annexed formula, are obtained, but could not be satisfactorily analysed. Contrary to the statement of Harries and Busse (A., 1896, i, 301), *o*-hydroxybenzylidenediacetophenone (Bablich and Kostanecki, A., 1896, i, 239; Cornelson and Kostanecki, A., 1896, i, 240) is produced by condensing acetophenone and salicylaldehyde by means of 10% sodium carbonate solution.

J. C. C.

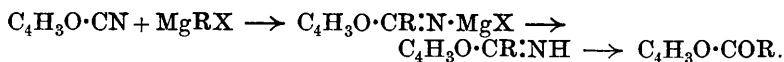
**Experimental Studies on Plant Pigments.** B. HARROW and W. J. GIES (*Proc. Soc. Expt. Biol. Med.*, 1918, **16**, 8—10).—Observations are reported on (a) flavones, a group of yellow pig-



ments characterised by the production, in their solutions, of intense yellowish-brown colour on the addition of aqueous ammonia, and of (b) anthocyanins, a group of red, violet, or blue pigments, which in solution change to bluish-green on the addition of acid. These pigments were obtained from tulips. Active (nascent) hydrogen reduces flavone to anthocyanin. The latter can be further reduced to a leuco-base, which in turn, by exposure to air, or more rapidly by addition of an oxidising agent, is reconverted into anthocyanin. Anthocyanin, isolated in a fairly pure condition by Willstätter's method, has been oxidised to flavone with the aid of hydrogen peroxide. Flavone thus obtained from anthocyanin can be reduced again to anthocyanin. Anthocyanin when extracted with alcohol made anhydrous with copper sulphate yields a red extract, whereas if the extraction is made with alcohol rendered anhydrous with calcium oxide, a green solution is obtained. Anthocyanin, prepared according to Willstätter's method and dissolved in absolute alcohol, was compared with phenolphthalein, and found to be its equal in point of delicacy. It is superior in that a change from alkali to acid is indicated by a sharp change from green to red, and not from red to no colour at all.

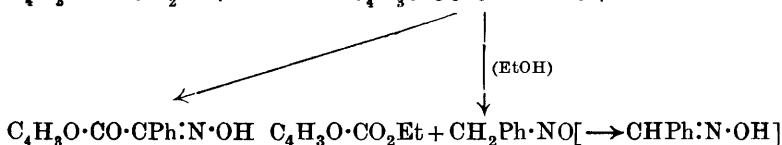
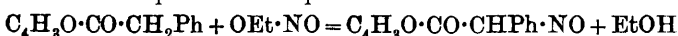
CHEMICAL ABSTRACTS.

**Furyl Alkyl Ketones.** K. MONOYA (*J. Pharm. Soc., Japan*, 1919, **447**, 357—401).—The relation between the constitution of furyl alkyl ketones and their optical properties, and also their action with sodium and alkyl nitrite, have been investigated. The ketones were prepared from furancarboxylonitrile (pyromuc-nitrile) and magnesium alkyl haloids in dry ether, the intermediate products being decomposed by heating with sulphuric acid and a little oxalic acid. Thus were prepared *furyl benzyl ketone*, plates, m. p. 47—48° (*oxime*, m. p. 125—126°; *semicarbazone*, m. p. 171—172°), *furyl methyl ketone*,  $D_4^{20}$  1.0977,  $n_D$  1.50177, *furyl ethyl ketone*,  $D_4^{25}$  1.0587,  $n_D$  1.49623, *furyl propyl ketone*,  $D_4^{14}$  1.0416,  $n_D$  1.49970, *furyl isobutyl ketone*,  $D_4^{16}$  1.0160,  $n_D$  1.49488, and *furyl isoamyl ketone*,  $D_4^{11}$  0.9988,  $n_D$  1.49260. The exaltation of the molecular refraction of the ketones increases with the molecular weight. During the preparation of the last two ketones, *ketimines* were isolated in the form of double compounds with ammonium chloride,  $2C_4H_3O \cdot C(:NH) \cdot C_4H_9, NH_4Cl$ , m. p. 285—291°, and  $2C_4H_3O \cdot C(:NH) \cdot C_5H_{11}, NH_4Cl$ , m. p. 268—270°. Since these are easily converted into the ketones by treatment with hydrochloric acid, the formation of the latter is represented by the scheme:



Ethyl pyromucate, pyromucic acid,  $\beta$ -benzaloxime, and oximino-deoxybenzofurcin are formed when furyl benzyl ketone is treated with ethyl nitrite and sodium in dry ether at  $-13^\circ$ ; the products are isolated by neutralising the mixture with 1% sodium hydroxide, extracting with ether, saturating the aqueous solution with carbon

dioxide, and then acidifying it with hydrochloric acid. The course of the decomposition is represented thus:

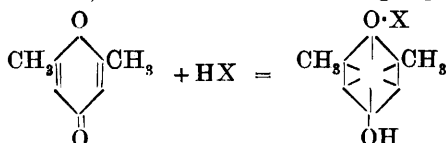


Furyl amyl ketone yields valeraldoxime, and the other ketones yield similar products when treated in this manner. By treatment with sodium and amyl nitrite, menthone yields  $\gamma$ -keto- $\beta\zeta$ -dimethyloctoic acid (semicarbazone, m. p. 151—152°).

#### CHEMICAL ABSTRACTS.

**Optical Chemical Notes on the Oxonium Salts of Pyrones and Thiopyrones.** A. HANTZSCH (*Ber.*, 1919, **52**, [B], 1535—1544).—The absorption curves of a number of pyroxonium salts are discussed.

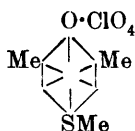
2:6-Dimethyl-1:4-pyrone shows the rudiments of an absorption band at about  $1/\lambda = 3600$  in concentrated alcoholic solutions, that is, in the region of the acetone band. This ketone band disappears when the pyrone is dissolved in concentrated sulphuric acid, the curves corresponding closely with those given by pyridinium salts. This is in accordance with Baeyer's formula for the pyroxonium salts (A., 1910, i, 763), the salt formation being represented thus:



Strange to say, the salts of 2:4:6-trimethylpyroxonium have a much greater absorptive power than those of the 4-methoxy-2:6-dimethyl series, that is, the methoxy-group is hypsochromic, and not an auxochrome, in this series. This still further emphasises the analogy between pyroxonium salts and pyridinium salts, for methoxylutidine salts are less absorptive than collidine salts (Purvis, T., 1909, **95**, 295; Baker and Baly, T., 1901, **91**, 1130).

2:6-Dimethyl-1:4-thiopyrone,  $\text{SC} \begin{array}{c} \text{CH}\cdot\text{CMe} \\ \text{CH}\cdot\text{CMe} \end{array} \text{O}$ , yellow needles, m. p. 145°, is obtained by the action of phosphorus pentasulphide on the corresponding pyrone in benzene. This forms colourless salts with the strong acids, but they are very easily hydrolysed.

That the salts contain a free thiol group is shown by the fact that methyl sulphate gives a salt which may be transformed into 2:4:6-trimethylpyrthionium perchlorate (annexed formula). The solutions of the thiopyrone in alcohol, water, or chloroform are yellow, but are cherry-red in ether or light petroleum and have different absorption bands. The highly coloured

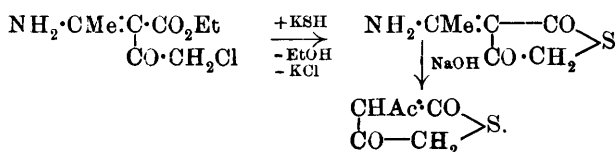


solutions may possibly contain an isomeride of the annexed formula. The salts have much weaker absorption in concentrated sulphuric acid, and the effect of replacing the  $\cdot\text{SH}$  group by the  $\cdot\text{SMe}$  group is to displace the bands towards the red. This is remarkable, for the analogous change in the pyrone series,  $\cdot\text{OH}$  to  $\cdot\text{OMe}$ , is not accompanied by any optical effect.

The paper concludes with a criticism of the tendency to formulate all manner of compounds as oxonium salts, for example, the additive compounds of ether with halogen acids, hydroferrocyanic acid, heteropoly-acids, trichloroacetic acid, and even other indifferent substances.

J. C. W.

**Synthesis of Thiophen Derivatives from Ethyl  $\beta$ -Amino-crotonate. II.** ERICH BENARY and L. SILBERSTROM (*Ber.*, 1919, 52, [B], 1605—1613. Compare A., 1915, i, 576).—For some unknown reason, a new supply of 33% potassium hydrosulphide solution has produced from ethyl  $\beta$ -amino- $\alpha$ -chloroacetyl crotonate a compound different to that originally described. The product is apparently  $\alpha$ -acetylthiotetronamide, for it may be hydrolysed by sodium hydroxide to  $\alpha$ -acetylthiotetronic acid (A., 1913, i, 892). It crystallises in long, pale yellow needles, m. p. 233°. The relationships are represented thus:



The original product, ethyl 4-hydroxy-2-methylthiophen-3-carboxylate, is always formed if the crotonate is shaken with a suspension of solid potassium hydrosulphide in alcohol. Some further reactions of the ester are now described.

When treated with sodium nitrite in glacial acetic acid, the ester yields *ethyl 3-keto-2-nitroimino-5-methyl-2:3-dihydrothiophen-4-carboxylate*,  $\text{S} < \begin{array}{c} \text{CMe} = \\ \text{C} \cdot \text{CO}_2\text{Et} \\ \text{C}(\text{N} \cdot \text{NO}_2) \cdot \text{CO} \end{array}$ , which separates in long, yellowish-green needles, decomp. 211°. This behaves as an acid, for it reddens litmus, forms an orange-coloured compound with ammonia,  $\text{C}_8\text{H}_8\text{O}_5\text{N}_2\text{S} \cdot \text{NH}_3$ , which dissolves in water, and gives precipitates of a red *lead* salt,  $\text{PbX}$ , and a brownish-red *silver* salt,  $\text{Ag}_2\text{X}$ , and also yields a reddish-brown *potassium* salt,  $\text{K}_2\text{X}$ , and a *di-p-nitrobenzoyl* derivative, greyish-green tablets, m. p. 162°. The corresponding *3-keto-2-nitroimino-5-methyl-2:3-dihydrothiophen-4-carboxylic acid*, made in the same way from the acid (*loc. cit.*), is a brown powder, decomp. above 100°, which forms a *potassium* salt,  $\text{K}_3\text{X}$ , and an explosive *lead* salt,  $(\text{C}_6\text{H}_3\text{O}_6\text{N}_2\text{S})_2\text{Pb}_3$ .

With amyl nitrite, however, the products are the normal oximes.

d\*



substances to be identical. The formula for the alkaloid is therefore  $C_{27}H_{43}O_8N$ . Certain corrections of the data recorded in the literature are given. The alkaloid crystallises with  $3.5H_2O$ , and has m. p.  $110^\circ$ . The hydrogen sulphate  $+ 2.5H_2O$  has m. p.  $250^\circ$  (decomp.); after becoming discoloured at  $210^\circ$ . The potassium salt has the composition  $C_{27}H_{41}O_8NK_2, EtOH$ , or, more probably,  $C_{27}H_{42}O_8NK, EtOK$ .

The hydrochloride forms anhydrous needles, m. p.  $247^\circ$ . The aurichloride from sabadinine has m. p.  $162^\circ$  (decomp.), whilst that from cevine has m. p.  $167$ — $168^\circ$  (decomp.). The *monobenzoyl* derivative forms a white, amorphous powder, m. p.  $195^\circ$  (decomp.), after much previous softening. H. W.

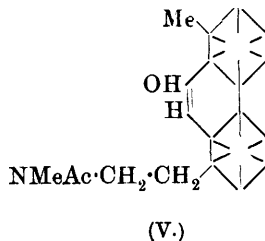
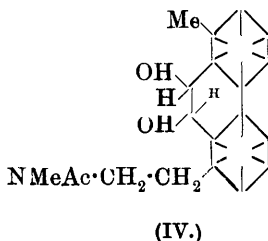
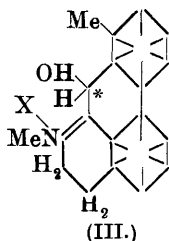
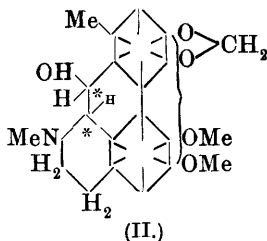
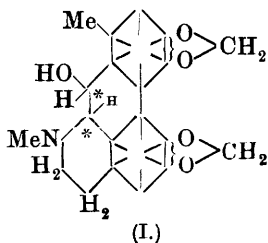
**Chelidoneum Alkaloids.** J. GADAMER (*Arch. Pharm.*, 1919, 257, 298—303).—Oxidation of the three chelidoneum alkaloids, chelidonine and  $\alpha$ - and  $\beta$ -homochelidonines, by means of mercuric acetate indicates that the former two are closely allied and that  $\beta$ -homochelidonine must be placed in the protopine group. Thus, both chelidonine and  $\alpha$ -homochelidonine give up two atoms of hydrogen, passing into intensely yellowish-red salts of dehydro-bases which are of quaternary character, but exhibit such a marked tendency to the formation of colourless carbinol bases that they are converted into these even by the action of ammonia. From the fact that the optical activity is considerably increased, it must be assumed that the double linking which is introduced occupies a position adjacent to an asymmetric carbon atom. The optical activity of  $\alpha$ -homochelidonine is of the same direction and order of magnitude as that of chelidonine, and the molecule contains, besides the two methoxyl groups, also a methylenedioxy-, a methylimino-, and an alcoholic hydroxyl group. On acylation it behaves similarly to chelidonine; by the action of acetic anhydride at a moderate temperature, acetylation occurs mainly at the oxygen atom (compare Tyrer, *Apoth.-Zeit.*, 1897, 442; Wintgen, A., 1901, i, 743), whilst at the boiling point it takes place almost exclusively at the nitrogen atom with elimination of water and ring-opening (compare Henschke, A., 1889, 62). On *O*-acetylation the optical activity is retained, whilst the *N*-acetyl compound is inactive.

When chelidonine methochloride or methosulphate is boiled with sodium hydroxide solution a strongly laevorotatory methine base and a small proportion of an apparently inactive methine base are formed.

On the basis of these observations, formula I is proposed for chelidonine and formula II for  $\alpha$ -homochelidonine, each of these formulæ containing two asymmetric carbon atoms, marked with an asterisk. On oxidation to a didehydro-base, the asymmetry of the carbon atom contiguous to the nitrogen atom disappears, an optically active compound of formula III being obtained. The ring-opening on acetylation at the boiling point must yield first a compound of formula IV, this losing water to form compound V, which

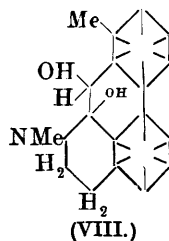
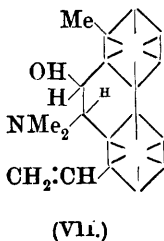
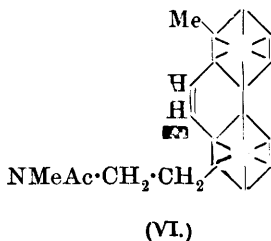


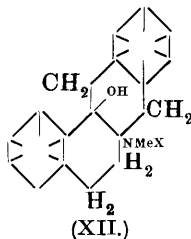
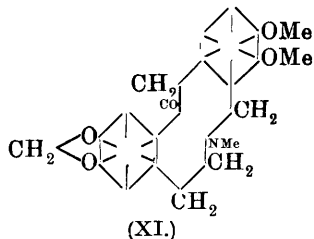
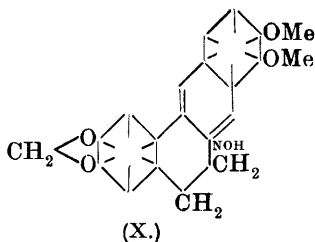
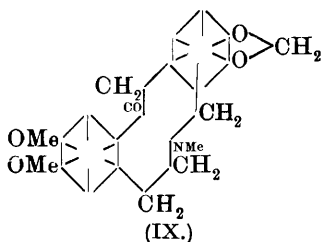
still contains  $1\text{H}_2\text{O}$  more than corresponds with an *N*-acetyl-anhydrochelidonine. Further loss of water is, however, less prob-



able than auto-oxidation and auto-reduction, which should yield a compound of formula VI, but the analytical results do not correspond. The *N*-acetyl derivative is always accompanied by a small proportion of a colourless, quinone-like compound, which gradually turns intensely red and is probably formed by oxidation. These conclusions are supported by the fact that the *O*-acetyl compound cannot be converted into the *N*-acetyl derivative by heating it, either alone or with acetic anhydride.

The levorotatory methine base obtained by methylation of chelidonine has probably the formula VII. On reduction, dihydrochelidonine is converted into chelidonine and, if the suggested formula is correct, two diastereoisomeric chelidonines should result, but their formation has not yet been verified. The free carbinol base must have the structure VIII. The position assumed for the methyl groups is not an entirely arbitrary one, since the alkaloids of the protopine group, which are to be referred to the same components (Bausteine), also contain at this place a side-chain of one carbon atom, this serving likewise to build up a heterocyclic ring.





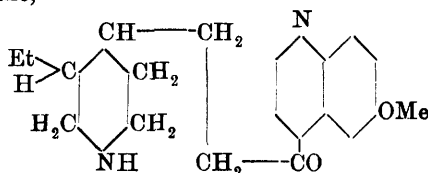
$\beta$ -Homochelidonine, which resembles protopine and cryptopine in its physiological action, also behaves like these bases towards mercuric acetate; thus, two hydrogen atoms are replaced by an oxygen atom, so that one molecule of the base reduces four molecules of mercuric acetate to mercurous acetate. The product of the oxidation is relatively readily soluble in hot water, giving a slightly alkaline solution. This behaviour and the isomerism of cryptopine and  $\beta$ -homochelidonine indicate that the two alkaloids differ only as regards the relative positions of the methylenedioxy- and the two methoxy-groups. Assuming for cryptopine Perkin's formula (IX) (compare T., 1916, **109**, 831), which renders evident its close relationship to berberinium hydroxide (X),  $\beta$ -homochelidonine must be represented by formula XI. Confirmation of this formula is furnished (1) by the action of phosphoryl chloride, which yields *iso*- $\beta$ -homochelidonine chloride, identical with dihydroberberine methochloride, and (2) by reduction to dihydro- $\beta$ -homochelidonine and conversion of the latter, by means of phosphoryl chloride, into the chloride of the *iso*-compound, which exhibits complete identity with tetrahydroberberine methochloride.

These results supply a confirmation of Perkin's formulæ for protopine and cryptopine, but an objection to the formulæ for the three bases is the possession of a ten-membered ring, the formation of which in the vegetable organism is as yet unknown. This objection may be removed by the assumption for the salts, which alone are formed in plants, of formula XII. Formula XI or IX would then result only by anhydride formation from the carbinol base produced by the action of alkali. In agreement with this assumption is the fact that, with protopine, cryptopine, and, especially,  $\beta$ -homochelidonine, in presence of ammonium chloride, precipitation of the bases by ammonia takes place either not at all or only after some time.

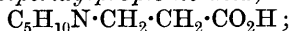
Replacement of the name  $\beta$ -homochelidonine by *allocryptopine* is recommended.

T. H. P.

**The Cinchona Alkaloids. XXI. Synthesis of Dihydroquinicine and  $\beta$ -4-Piperidylpropionic Acid.** PAUL RABE and KARL KINDLER (*Ber.*, 1919, **52**, [B], 1842—1850. Compare A., 1919, i, 34).—I. *Synthesis of Dihydroquinicine (Dihydroquinotoxine)*.—Ethyl quinate and ethyl *N*-benzoylhomocincholeupionate (*ibid.*) are condensed by means of sodium ethoxide in benzene to form a  $\beta$ -ketonic ester, which is deprived of the benzoyl and carbethoxyl groups by boiling with 17% hydrochloric acid, thus giving dihydroquinicine,



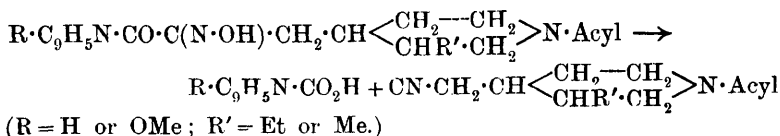
II. *Synthesis of  $\beta$ -4-Piperidylpropionic Acid*.—4-Methylpyridine is heated with chloral and zinc chloride at 85—90° for several hours, and thus converted into " $\gamma$ -chloralpicoline" [ $\gamma\gamma\gamma$ -trichloro- $\alpha$ -4-pyridylpropan- $\beta$ -ol],  $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{C}_5\text{H}_4\text{N}$ , glistening crystals, m. p. 166° (corr.); *platinichloride*, orange needles, m. p. 250° (corr., decomp.), *aurichloride*, yellow crystals, m. p. 189° (corr., decomp.). This compound is mixed with ice-cold alcoholic potassium hydroxide, and the temperature then allowed to rise, when hydrolysis proceeds vigorously, the product being  $\beta$ -4-pyridylacrylic acid,  $\text{C}_5\text{H}_4\text{N}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ , pale reddish-brown crystals, m. p. 296° (corr., decomp.); *hydrochloride*,  $1\text{H}_2\text{O}$ , large, brown crystals, m. p. 243—244° (corr.), *aurichloride*, yellow needles, m. p. 235° (corr., decomp.). The acid is reduced by sodium in boiling amyl alcohol to  $\beta$ -4-piperidylpropionic acid,



the acid was not isolated, but converted into the *ethyl* ester, b. p. 145°/15 mm., *platinichloride*, orange crystals, m. p. 190° (corr., decomp.).

J. C. W.

**Preparation of Nitriles from Quinotoxines.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 313321; from *Chem. Zentr.*, 1919, iv, 499).—Oximinoacidyl derivatives of dihydroquinotoxine are treated with acidylating agents in the presence of alkali. Reaction occurs in accordance with the scheme:



Cinchotoxine is converted by benzoyl chloride in the presence of

alkali into a *benzoyl* derivative, m. p.  $124^{\circ}$ , which, when treated with amyl nitrite and sodium alkyloxide, yields a crystalline *oximino*-derivative, m. p.  $175-177^{\circ}$ ; the yellowish-red solution of the latter in sodium hydroxide solution (5%) is transformed by toluene-*p*-sulphonyl chloride at  $45^{\circ}$  into *benzoylcincholeupono-nitrile*, colourless crystals, m. p.  $62^{\circ}$ . *Acetylcinchotoxine* is formed as a pale yellow, viscous mass by the treatment of cinchotoxin (quinicine) with acetyl chloride, and, without being further purified, is converted into *oximinoacetylcinchotoxine*, from which *acetylmero-quinenonitrile*, almost colourless, viscous oil, is prepared by the action of benzoyl chloride and sodium hydroxide solution (5%). The nitriles are intended as initial materials for pharmaceutical preparations.

H. W.

**The Oxidation of Morphine.** CONSTANTIN KOLLO (*Bul. Soc. chim. România*, 1919, 1, 3—9).—Solutions of morphine hydrochloride when sterilised in an autoclave at  $120^{\circ}$  undergo some decomposition, as shown by the brown colour produced in the liquid. The change occurring is the formation of oxydimorphine ( $\psi$ -morphine) and morphine oxide in the proportion of 9:1, together with traces of a base said to be methylamine. The percentage of morphine decomposed increases with the temperature to which the solution is heated.

It is suggested that morphine hydrochloride undergoes partial dissociation, and that in the free morphine the group :NMe reacts with the water, giving methylamine and hydrogen peroxide, the latter then acting as an oxidising agent.

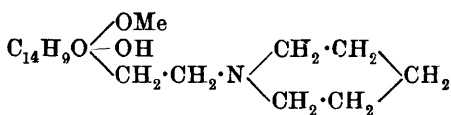
W. G.

**Morphine Alkaloids. VI. The Relative Stability of the Nitrogen Ring in Morphine.** JULIUS VON BRAUN (*Ber.*, 1919, 52, [B], 1999—2011).—It has recently been shown (A., 1918, i, 184, 268) that the gradations of stability exhibited by six of the seven classes of bases which have been examined from the point of view of the rupturing of the cyclic system are the same whether the action be effected by Hofmann's method or by cyanogen bromide. Dihydroindole appears to be an exception, since it proves to be one of the most stable systems in the Hofmann degradation, but one of the weakest towards cyanogen bromide. The present communication contains an account of the behaviour of a number of substances containing the grouping, aromatic nucleus, C·C·N, which is present in the morphine molecule. This appears to be extraordinarily resistant to cyanogen bromide, but to be attacked with remarkable ease by bases.

The nomenclature of some of the substances which have been obtained offers certain difficulties, to overcome which the author proposes to designate the group,  $C_{14}H_9O(OMe)(OH) \cdot CH_2 \cdot CH_2-$ , methylmorphimethyl.

*Norcodeinium piperidinium iodide*, m. p.  $272^{\circ}$ , is prepared by the action of norcodeine on  $\alpha$ -di-iodopentane in alcohol, or, preferably, in chloroform (the *platinichloride* is a crystalline powder,

m. p. 215°; the corresponding *dihydronorcodeinium piperidinium iodide* has m. p. 271°), and is converted by cold aqueous sodium hydroxide solution into *methylmorphimethylpiperidine* (annexed

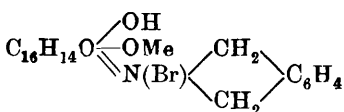


formula), stout rods, m. p. 93—94° (the hygroscopic *hydrochloride*, the *platinichloride*, m. p. 174°, the oily *methiodide*, and the *acetyl* derivative, m. p.

87°, are described). It cannot readily be shown that the disruption of the nitrogen atom has occurred from the morphine and not from the piperidine half of the molecule by the use of acetic anhydride, but the required evidence is readily furnished by the application of cyanogen bromide to the acetyl derivative, which yields *ε-bromoamylcyanoacetylmethylmorphimethylamide*,

$\text{C}_{14}\text{H}_9\text{O}(\text{OMe})(\text{OAc}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{N}(\text{CN})[\text{CH}_2]_5\text{Br}$ ,  
colourless leaflets, m. p. 133—134°.

Norcodeine and *o*-xylylene bromide similarly yield *norcodeinium-dihydroisindolium bromide* (annexed formula), long needles, m. p.



262° (*platinichloride*, m. p. 233°), which is transformed by alkali into *methylmorphimethyldihydroisindole*, m. p. 110°, the salts of which show little tendency to crystallise. The crystalline *acetyl*

derivative, shining leaflets, m. p. 146°, yields, however, a *hydrochloride*, colourless leaflets, m. p. 224°, and a *methiodide*, colourless leaflets, m. p. 163°. The course of fission is already established by the nature of the product, and is confirmed by the action of cyanogen bromide on the acetyl derivative, which yields *ω-bromoxylylcyanoacetylmethylmorphimethylamine*, colourless crystals, m. p. 153°.

The interaction of norcodeine and  $\beta\beta'$ -di-iodoethyl ether leads to the formation of *norcodeinium-morpholinium iodide*, long needles, m. p. 255—256° (*platinichloride*, m. p. 216°), which is converted by alkali into *methylmorphimethylmorpholine*; since the latter is oily and does not yield well-crystallised salts, it was identified as the *acetyl* derivative, m. p. 118—120° (*platinichloride*, m. p. 177°). Cyanogen bromide transforms the acetyl compound into an oily product, which doubtless consists mainly of the expected bromo-compound, but could not be isolated in the pure state.

H. W.

**Ormosine and Ormosinine, Two New Alkaloids from *Ormosia dasycarpa*.** KURT HESS and FRITZ MERCK (*Ber.*, 1919, 52, [B], 1976—1983).—Ormosine has been previously isolated by Merck from *Ormosia dasycarpa*, Jacks, a leguminous plant growing in Venezuela. Its physiological relationship to the morphine alkaloids has been demonstrated by Harnack, but the authors find that it is not allied chemically to these substances, and, indeed,

occupies a unique position among alkaloids. In addition, they have isolated ormosinine from the same source, the yield of the former amounting to 0.15% and of the latter to 0.023% of the dried seeds; these substances, however, only represent a fraction of the total alkaloidal content.

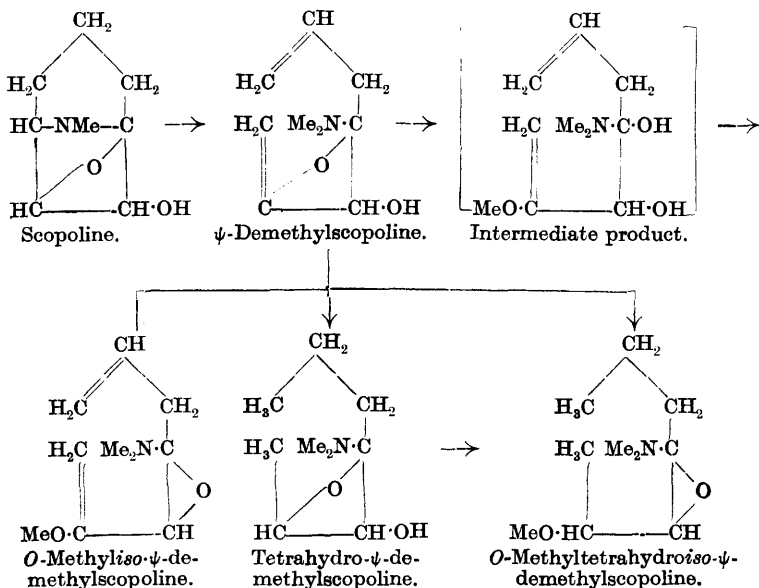
Isolation of the alkaloids is effected by extracting the crushed seeds with alcohol, evaporation of the solvent in a vacuum, and extraction of the residue with water; the aqueous extract is made alkaline with ammonia and extracted with ether. The ethereal solution is shaken with powdered sodium carbonate, after which the solvent is removed, leaving a crystalline residue, from which ormosinine is isolated by taking advantage of its sparing solubility in alcohol, whilst ormosine separates from the alcoholic solution on addition of water.

*Ormosine*,  $C_{20}H_{33}N_3$ , crystallises with 3—4H<sub>2</sub>O in long needles, m. p. 85—87°, and is readily soluble in alcohol or chloroform. When preserved over sulphuric acid, it loses its water of crystallisation and forms a colourless, gummy mass, which again becomes crystalline when brought into contact with water. It is sensitive towards rise in temperature, and, at 100°, is converted into a viscous oil, which does not recombine with water. With methyl iodide, it gives an abnormally constituted *methiodide*,  $C_{24}H_{45}N_3I_2$ , long needles, m. p. 245—250° (slow decomp.). The *picrate* has m. p. 178° (decomp.). The *hydrochloride*, *hydrobromide*, and *aurechloride* are amorphous. The *aurechloride* of the *methochloride*,  $C_{24}H_{45}N_3Cl_2 \cdot 2AuCl_3$ , forms yellow crystals, which change at 90°.

*Ormosinine*,  $C_{20}H_{33}N_3$ , crystallises in well-defined, anhydrous cubes and short prisms, m. p. 203—205°. It yields a normally constituted *methiodide*,  $C_{21}H_{36}N_3I$ , colourless needles, m. p. 245° (slow decomp.), and a *picrate*,  $C_{32}H_{39}O_{14}N_9 \cdot 4H_2O$ . H. W.

**Scopoline. IV. Fission of Scopoline by Hofmann's Method of Degradation and Elucidation of the Constitution of Scopoline.** KURT HESS (*Ber.*, 1919, 52, [B], 1947—1975).—Previous investigations (A., 1918, i, 404, and previous abstracts) have largely elucidated the constitution of scopoline, leaving in doubt, however, the mode of attachment within the molecule of one valency of one of the oxygen atoms. In the hope of deciding this point, the author has applied Hofmann's method to scopoline. Reaction, however, occurs abnormally, since the product,  $\psi$ -demethylscopoline, contains two double bonds, as is evidenced by its ready conversion into a tetrahydro-derivative. Moreover, the process throws no light on the point in question, since the oxygen linking appears to remain intact. When, however,  $\psi$ -demethylscopoline is further subjected to the Hofmann degradation, it gives *O*-methyliso- $\psi$ -demethylscopoline, the ammonium base yielding the tertiary amine and methyl alcohol, which adds itself at the ethylene oxide group. Elimination of water occurs from the methylated polyhydroxy-alcohol in such a manner as to form a new ethylene oxide group.

This view is strengthened by the formation of a similarly constituted compound from tetrahydro- $\psi$ -demethylscopoline, which is also produced by the reduction of *O*-methyliso- $\psi$ -demethylscopoline itself. The most ready explanation of these reactions lies in the hypothesis that the ethereal oxygen atom is directly united to that carbon atom to which the nitrogen group is attached, since, if it were attached to one of the other possible carbon atoms, it is difficult to see why the oxygen bridge should be disturbed by a process which only affects the amino-group. The reactions are consequently shown by the schemes:



Corresponding with the two asymmetric carbon atoms of  $\psi$ -demethylscopoline, the latter is found to exist in two diastereoisomeric racemic forms ( $\alpha$ - and  $\beta$ -), both of which have been isolated and used in the series of degradations. During hydrogenation, a third asymmetric carbon atom is developed, so that yet another isomeride is formed.

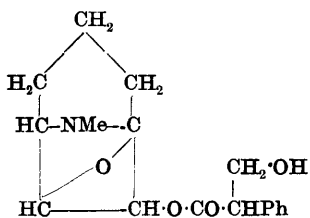
Scopoline methiodide is converted into the corresponding hydroxide, which is distilled under diminished pressure, whereby an oil, b. p. 118—121°/9 mm., is obtained in good yield, which consists of a mixture of approximately equal amounts of  $\alpha$ - and  $\beta$ - $\psi$ -demethylscopoline. The  $\alpha$ -form crystallises in needles or prisms, m. p. 67—69° (*picrate*, prismatic needles, m. p. 152—153°; *methiodide*, m. p. 248° [decomp.]; *benzoyl* derivative, indistinct, crystalline needles, m. p. 120°, the *hydrochloride* of which [+3EtOH] has m. p. 214° [decomp.], after much previous softening). The  $\beta$ -form has b. p. 135—140°/15—16 mm. (*picrate*, large, cubic crystals, m. p. 205° [decomp.]; the *methiodide* is oily).

Reduction of  $\alpha\psi$ -demethylscopoline by hydrogen in the presence of colloidal platinum yields a product, b. p.  $143\text{--}145^\circ/30$  mm., which solidifies completely to a mass of long needles, but which is found to be a mixture of two stereoisomerides, since it gives two *picrates*, m. p.'s  $182^\circ$  and  $128^\circ$  respectively, and two *methiodides*, m. p.  $209^\circ$  and oily. The corresponding  $\beta$ -base also appears to yield two stereoisomeric *tetrahydro- $\beta\psi$ -demethylscopolines* (b. p. of mixture  $135^\circ/27$  mm.), the *methiodides* of which are oily. *O-Methyltetrahydroiso- $\alpha\psi$ -demethylscopoline* is obtained by Hofmann's method from the tetrahydro- $\alpha$ -base, and forms an oil, b. p.  $122\text{--}125^\circ/17$  mm., which partly crystallises when preserved, and probably consists of a mixture of isomerides; the *picrate* has m. p.  $163^\circ$ . The corresponding  $\beta$ -derivative has b. p.  $126\text{--}130^\circ/23$  mm. (*picrate*, m. p.  $183\text{--}184^\circ$ ; *platinichloride*, hexagonal crystals, m. p.  $200^\circ$  [decomp.]).

The degradation of  $\alpha$ - and  $\beta\psi$ -demethylscopoline does not occur very smoothly, and in addition to *O-methyliso- $\alpha\psi$ -demethylscopoline*, pale yellow oil, b. p.  $123^\circ/14$  mm., and *O-methyliso- $\beta\psi$ -demethylscopoline*, viscous, yellow oil, b. p.  $140^\circ/28$  mm., a highly refractive volatile oil,  $\text{C}_7\text{H}_8\text{O}_2$ , of characteristic odour, b. p.  $88\text{--}92^\circ/11$  mm., is obtained. A *picrate*, needles, m. p.  $142\text{--}143^\circ$ , was isolated from the product of the degradation of the mixed bases.

The oxygen bridge in  $\alpha\psi$ -demethylscopoline, unlike that in scopoline itself (A., 1916, i, 286), does not appear to be opened by treatment with hydrogen bromide in glacial acetic acid solution, the products of the action being the *hydrobromide* of the original base, prisms, m. p.  $250^\circ$  (decomp.), and resinous matter.

Attempts further to degrade the tetrahydro-*O*-methyliso- $\psi$ -demethylscopolines were unsuccessful, the



bases being recovered unchanged.

As a consequence of the work on scopoline, the annexed formula may now be ascribed to scopolamine.

H. W.

**Strychnos Alkaloids. XXV. Rearrangement of Strychninolone into Isomeric Forms.** HERMANN LEUCHS and WALTER BENDIXSOHN (*Ber.*, 1919, **52**, [B], 1443—1453. Compare A., 1914, i, 861).—When the  $\alpha$ -form of strychninolone,  $\text{C}_{19}\text{H}_{18}\text{O}_3\text{N}_2$ , is shaken with 0.5*N*-sodium hydroxide for a few days, about 80% of it is changed into strychninolone-*b*, massive crystals, m. p.  $228^\circ$ ,  $[\alpha]_D^{20} - 37.3^\circ$ . The alkali contains about 6% of the by-product,  $\text{C}_{19}\text{H}_{20}\text{O}_4\text{N}_2$ , m. p.  $235\text{--}270^\circ$ ,  $[\alpha]_D^{20} + 21.5^\circ$ , which was also formed during the fission of strychninolic acid. A similar transformation is effected by heating the  $\alpha$ -form with methyl-alcoholic ammonia in a sealed tube. The products are the *b*-form, a new isomeride which is less soluble in methyl alcohol, namely, *strychninolone-c*, hexagonal prisms or pointed and twinned leaflets, m. p.  $251\text{--}252^\circ$ ,



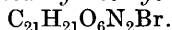
$[\alpha]_D^{13} - 176.1^\circ$ , and two isomeric amines. These are *aminodihydrostrychninolone-I*,  $C_{19}H_{21}O_3N_3 \cdot H_2O$ , polyhedric tablets or columns, m. p.  $185-191^\circ$  (decomp.), which forms a sparingly soluble *nitrate*, m. p.  $261-263^\circ$  (decomp.),  $[\alpha]_D^{15} - 51.6^\circ$ , and a *phenylcarbamide*,  $C_{26}H_{26}O_4N_4$ , m. p.  $240-241^\circ$ , and again at  $295-300^\circ$ , and also *aminodihydrostrychninolone-II*, stout needles, m. p.  $236-239^\circ$  (decomp.),  $[\alpha]_D^{14} - 66.6^\circ$ , which forms a soluble *nitrate*.

When strychninolone-*b* is covered with 12*N*-hydrochloric acid, it changes into the salt of an *amino-acid*,  $C_{19}H_{20}O_4N_2 \cdot 4H_2O$ , broad needles, m. p.  $239-240^\circ$  (decomp.), which is identical with the strychninolone-hydrate-II, already described (A., 1910, i, 768). Strychninolone-*b* also forms an *acetate*,  $C_{21}H_{20}O_4N_2$ , when heated with acetic anhydride and sodium acetate. This crystallises in prisms with 1MeOH, m. p.  $140^\circ$  (decomp.), and then  $214^\circ$ ,  $[\alpha]_D^{20} - 37.6^\circ$ , and may be formed by heating acetylstrychninolone-*a* with acetic anhydride.

J. C. W.

### Strychnos Alkaloids. XXVI. Degradation of Bromostychnine and Dihydrostrychninonic Acid, and the Bromination of the Fission Products of Strychnine.

HERMANN LEUCHS and DOROTHEA RITTER (*Ber.*, 1919, 52, [B], 1583-1593). —Bromostychnine (Beckurts, A., 1885, 911) is most conveniently made by adding bromine water to strychnine dissolved in hydrobromic acid, for it separates as the hydrobromide (solubility at  $15^\circ$ , 1%), leaving the salt of the unchanged base in solution. When oxidised by permanganate at  $-10^\circ$  to  $15^\circ$  in acetone solution, it yields bromostychninonic acid (soluble in chloroform; A., 1910, i, 766) and insoluble *bromodihydrostrychninonic acid*,



This crystallises in minute, hexagonal leaflets, m. p.  $310^\circ$  (decomp.),  $[\alpha]_D^{20} - 19.7^\circ$  (in 0.1*N*-sodium hydroxide), may also be obtained by brominating dihydrostrychninonic acid, and is gradually hydrolysed by *N*-alkali hydroxide in the cold to glycollic acid and a *compound*,  $C_{19}H_{17}O_3N_2Br$ , which crystallises from alcohol in slender needles, m. p.  $273^\circ$ ,  $[\alpha]_D^{20} - 24.2^\circ$ .

Dihydrostrychninonic acid, obtained in 6% yield by oxidising strychnine with permanganate in boiling acetone, is hydrolysed by *N*-alkali hydroxide to two isomerides, according to the conditions. In the cold, the product is *isostychninolone-I*,  $C_{19}H_{18}O_3N_2$ , colourless pyramids, m. p.  $246-247^\circ$ ,  $[\alpha]_D^{20} + 46.4^\circ$ , which yields the above compound,  $C_{19}H_{17}O_3N_2Br$ , on bromination. At  $100^\circ$ , the product is *isostychninolone-II*, long, woolly needles, not molten at  $310^\circ$ ,  $[\alpha]_D^{20} - 126^\circ$ , giving a cornflower-blue colour with chromic and sulphuric acids, and a very sparingly soluble *bromo-derivative*, m. p.  $280^\circ$ .

Strychninonic acid yields the same acid on bromination as bromostychnine gives on oxidation, namely, bromostychninonic acid. The *methyl* ester of this,  $C_{22}H_{21}O_6N_2Br$ , has m. p.  $230-231^\circ$ , and the *ethyl* ester, m. p.  $247^\circ$  (corr.). The acid is reduced by sodium amalgam to *bromostychninonic acid*,  $C_{21}H_{21}O_6N_2Br$ , minute prisms,

decomp. 265—270°, which is gradually hydrolysed by *N*-sodium hydroxide to glycollic acid and bromostychninolone-*a* (below).

The *a*- and *b*-forms of stychninolone yield on bromination *bromostychninolone-a*,  $C_{19}H_{17}O_3N_2Br$ , stout tablets, m. p. 254—256°,  $[\alpha]_D^{20} - 62.2^\circ$ , and *bromostychninolone-b*, stout prisms or tablets, m. p. 233—235°,  $[\alpha]_D^{20} - 72.8^\circ$ . J. C. W.

**Synthesis of 2-*n*-Butylpyrrolidine. Remarks on the Work of E. Blaise and Houillon on the Transformation of the Higher Alkylenediamines into Cyclic Mono-imines.**

KURT HESS (*Ber.*, 1919, **52**, [B], 1636—1641).—2-Pyrrol propyl ketone (Oddo, A., 1910, i, 426) is reduced by sodium and alcohol to  $\alpha$ -2-pyrrolidylbutyl alcohol (A., 1916, i, 68), the constitution of which has been proved (A., 1917, i, 351, 352), and this is heated with hydriodic acid (D 2.0) and red phosphorus at 125—135°. 2-*n*-Butylpyrrolidine is a colourless oil, b. p. 154—156°/753 mm., which has a very similar odour to coniine, and is only sparingly soluble in water. The *platinichloride* forms stout prisms, m. p. 178°, and the *aurichloride* is an unstable, egg-yellow, flocculent powder, m. p. 145°. When heated with formaldehyde and formic acid, the base yields 1-methyl-2-*n*-butylpyrrolidine, b. p. 154—155°/15 mm., which forms a *platinichloride*, long, prismatic tablets, m. p. 215°, and an *aurichloride*, m. p. 190°.

The base described by Blaise and Houillon as 2-*n*-butylpyrrolidine (A., 1906, i, 692) must have had some other constitution.

J. C. W.

**Pyrrolidine Derivatives. V. Preparation of the Three Hydroxyprolines which are Stereoisomerides of the Natural Hydroxyproline.** HERMANN LEUCHS and KARL BORMANN (*Ber.*, 1919, **52**, [B], 2086—2097).—The work is a continuation of that described previously (Leuchs and Brewster, A., 1913, i, 449).

*dl*-Hydroxyproline (*a*) is resolved by crystallisation of the quinine salt of its phenylcarbamide, as described previously; the specific rotation of the synthetic *l*-hydroxyproline (*a*) in aqueous solution cannot be raised above  $-75.7^\circ$ , a value which agrees well with that recorded previously, but is lower than the sole datum ( $-81^\circ$ ) for the natural acid. *d*- $\gamma$ -Hydroxyprolinephenylcarbamide (*a*) has m. p. 175°,  $[\alpha]_D^{27} + 37^\circ$  (in water as ammonium salt); *d*-hydroxyproline (*a*) has m. p. about 274°,  $[\alpha]_D^{23} + 75.2^\circ$  in aqueous solution. The corresponding *hydantoin* has m. p. 130—131° (anhydrous), ca. 70° (+ 2H<sub>2</sub>O),  $[\alpha]_D^{25} + 49.2^\circ$ , for the anhydrous substance in water.

*dl*- $\gamma$ -Hydroxyprolinephenylcarbamide (*b*) is similarly resolved by means of quinine, as previously described; *l*- and *d*-hydroxyproline (*b*) have now been obtained in the crystalline form, slender needles, m. p. 238—241° (decomp.),  $[\alpha]_D^{18} - 58.1^\circ$  and  $+58.6^\circ$  respectively.

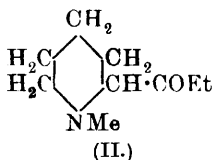
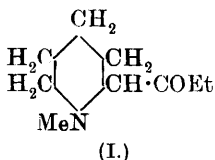
The product obtained by racemising the natural hydroxyproline with barium hydroxide appears to be identical with that obtained

by mixing equal weights of *l*-hydroxyproline (*a*) and *d*-hydroxyproline (*b*); it appears that a change of configuration only occurs at the  $\alpha$ -carbon atom, whilst the  $\gamma$ -carbon atom remains unaffected.

Derivatives of *dl*-hydroxyproline (*a*) and (*b*) with phenylthiocarbimide are described, but are unsuitable for purposes of resolution owing to the ease with which they pass into anhydrides which are either thiohydantoin or thioazlactones;  *$\gamma$ -hydroxyproline-phenylthiocarbimide* forms nodular crystals, and when crystallised from warm water or heated at 63° readily gives the corresponding *anhydride*, slender needles, m. p. 145—148°; its m. p. is the same as that of the anhydride;  *$\gamma$ -hydroxyproline-phenylthiocarbimide* (*b*), m. p. 155—156°, is rather more stable than the *a*-derivative. The corresponding *anhydride* crystallises in small needles, m. p. 146—148°.

H. W.

**The Asymmetric, Tervalent Nitrogen Atom. II. New Transformations of *dl*-Methylconhydrinone and the Conversion of *d*-Conhydrinone into *dl*- $\alpha$ -2-Pyrrolidylbutan- $\beta$ -one.** KURT HESS (*Ber.*, 1919, **52**, [B], 1622—1636. Compare A., 1919, i, 345).—In the former paper, it was shown that  $\alpha$ -1-methyl-2-piperidylpropan- $\alpha$ -one exists in two stereoisomeric forms, methyl-*isopelletierine* (I) and methylconhydrinone (II).



A further proof of the close relationship between these bases is now given, namely, the fact that when their hydrazones are boiled with sodium ethoxide solution they both yield *dl*-methylconiine.

In the further elucidation of this unusual case of isomerism, it is found that during changes at the asymmetric nitrogen atom, the particular configuration is preserved, but that changes at the propyl residue, that is, at the asymmetric carbon atom, lead to the same products in both cases.

As a reaction of the former type may be mentioned the dimethylation by means of ethyl azodicarboxylate. This leads to the production of *isopelletierine* on the one hand and *dl*-conhydrinone, b. p. 93—94°/10 mm., on the other. Furthermore, the ethylurethane of *d*-conhydrinone (*loc. cit.*) is isomeric with the *ethylurethane* of *isopelletierine*, this having now been obtained as a viscous oil, b. p. 165—170°/13 mm., by the action of ethyl chloroformate on the base in ether, under the influence of powdered potassium carbonate.

A most remarkable difference between these isomeric ethylurethanes is described. When boiled with aqueous-alcoholic sodium hydroxide, the *isopelletierine* derivative is slowly hydrolysed to *isopelletierine* and resinous products, whereas the *d*-conhydrinone

derivative is quickly and almost quantitatively converted into dl- $\alpha$ -2-pyrrolidylbutan- $\beta$ -one (annexed formula). This oil has b. p. 95—97°/10 mm., responds readily to the pine-shaving test, forms a *picrate*, bundles of needles, m. p. 155°, is converted by heating with formaldehyde and formic acid into  $\alpha$ -1-methyl-2-pyrrolidylbutan- $\beta$ -one, b. p. 112—115°/22 mm. (*hydrochloride*, m. p. 153°; *platinichloride*, m. p. 205°; *methiodide*, long spikes, m. p. 213—215°), and yields a *hydrazone*, b. p. 135—140°/15 mm., which is reduced by heating with sodium ethoxide solution at 150—170° to 2-butylpyrrolidine (see this vol., p. 85). J. C. W.

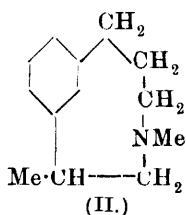
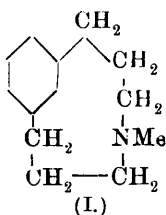
**Additive Compounds of Acyl Chlorides and Tertiary Amines.** KARL FREUDENBERG and DANIEL PETERS (*Ber.*, 1919, **52**, [B], 1463—1468).—In many cases, chloroform is an excellent medium in which to study reactions between acyl chlorides and tertiary amines, for the additive compounds readily separate, leaving such by-products as the amine hydrochlorides and dehydracetic acid in solution, and, furthermore, there is much less danger of the precipitate absorbing atmospheric moisture during filtration than when ether is used as the diluent (compare Dehn, A., 1912, i, 833; 1914, i, 1169). The true additive compounds are extremely sensitive to water and alcohol, especially in those cases in which intermolecular expulsion of hydrogen chloride is possible, and this is why so few genuine compounds of this type have been described.

Oxalyl chloride and pyridine form a compound in the ratio 1:2 (Jones and Tasker, P., 1908, **24**, 271), which separates in yellow, sandy crystals and evolves carbon monoxide and dioxide on exposure to moist air. Acetyl chloride and pyridine unite in the ratio 1:1 (Dennstedt and Zimmerman, A., 1886, 368), the compound dissolves in the chloroform if moisture is allowed to enter, and reacts with alcohol to form pyridine hydrochloride and ethyl acetate. The compound given by hexamethylenetetramine and benzoyl chloride is also decomposed by alcohol, which Hartung overlooked when he spoke of it as being somewhat soluble in this medium (A., 1892, 1173). J. C. W.

### Ring Closure in the Meta-position in the Benzene Series.

**I. Reduction of Julolidine Methochloride.** JULIUS VON BRAUN and LUDWIG NEUMANN (*Ber.*, 1919, **52**, [B], 2015—2019).—It has been shown previously (von Braun, Heider, and Wyczatkowska, A., 1919, i, 40) that the reduction of julolidine methochloride by sodium amalgam leads to the formation of a base,  $C_{13}H_{19}N$ . The latter has now been isolated as a colourless oil, b. p. 87—89°/0.01 mm., which can be preserved unchanged in a closed vessel (the methiodide has m. p. 178° instead of 200°, as previously recorded). When this is converted into its methiodide, treated with silver oxide, and the product is distilled under greatly

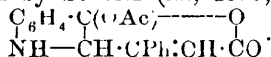
diminished pressure, two fractions are obtained: (1) unchanged base mixed with a certain amount of an unsaturated base, and (2) an oxy-base,  $C_{14}H_{23}ON$ , syrupy liquid, b. p.  $145-147^{\circ}/0.01$  mm. The *hydrochloride*, *platinichloride*, *picrate*, and *methiodide* of the latter are oily, but the *platinum* salt of the methochloride forms orange needles, m. p.  $165^{\circ}$ . The nitrogen atom of the base, like that of the original amine, is not attached to the aromatic nucleus, neither is oxygen present as phenolic hydroxyl. In confirmation of these facts, it is found that only *isophthalic* acid is formed when it is oxidised. It follows, therefore, that the base  $C_{13}H_{19}N$  must contain the complex  $C_6H_{12}NMe$  in the form of a closed chain united to two carbon atoms of the benzene nucleus which are in the meta-position to one another. The structure of the complex can be deduced with considerable probability from the following facts: (1) the nitrogen is probably in the  $\gamma$ -position to the benzene nucleus, since attempts to apply Hofmann's process to the degradation of the oxy-base were unsuccessful, and (2) the production of a tertiary hydroxy-amine instead of an unsaturated amine in Hofmann's reaction is only probable if a primary alcoholic group can be developed. The grouping



$-CH_2 \cdot CH_2 \cdot CH_2 \cdot NMe \cdot CH_2-$  is therefore probably present in the amine,  $C_{13}H_{19}N$ , and the annexed formulæ are thus possible. The second of these is, however, very improbable, since the corresponding hydroxy-base would show a great tendency to eliminate water and form a methylated styrene complex, and since, also,  $\alpha$ -methyl-lilolidine, which is very analogously constituted to julolidine, does not yield a trace of a base analogous to  $C_{13}H_{19}N$  when its methochloride is reduced.

H. W.

**The Acetyl Derivative of  $\beta$ -Indoxylcinnamic Acid.** RUD. WEGSCHIEDER (*Ber.*, 1919, **52**, [B], 1705).—The acetyl derivative obtained by Scholtz (*A.*, 1919, **1**, 96) may be represented by the formula



J. C. W.

**Modification of Skrap's Synthesis for Preparing Quinoline Bases: their Conversion into Stannichlorides.** J. G. F. DRUCE (*Chem. News*, 1919, **119**, 271-273).—The method adopted for the synthesis of quinoline from aniline stannichloride (*A.*, 1918, **1**, 535) has been applied successfully, although with diminished yields, to the synthesis of homologues of quinoline. Thus *o*-, *m*-, and *p*-toluidine stannichlorides treated with glycerol and sulphuric acid heated at  $120^{\circ}$  for two to three hours and then diluted and diazotised gave, respectively, 8-, 7-, and 6-methylquinoline in yields varying from 25% with the meta- to 70% with the para-compound.

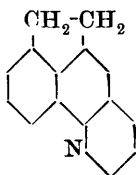
On the other hand, *m*- and *p*-phenylenediamine stannichlorides gave extremely poor yields of the phenanthrolines. The stannichlorides of the methylquinolines were prepared by dissolving crystalline stannic chloride in hydrochloric acid solutions of the bases, and they crystallised out on cooling. 6-Methylquinoline stannichloride forms white plates, m. p. 248°, 7-methylquinoline stannichloride, pale yellow needles, m. p. 229°, and 8-methylquinoline stannichloride, white needles, m. p. 252° (with decomp.). *m*-Toluidine stannichloride, prepared in an analogous fashion, formed pearly-white plates, soluble in cold water and alcohol, m. p. 76°. *m*-Toluidine stannichloride crystallised in pale pink, nacreous plates, m. p. 284°. A rapid method for the estimation of chlorine in these and other tin salts of aliphatic and aromatic bases was devised, consisting in simple titration with *N*/10-sodium hydroxide, using phenolphthalein as indicator. Good results were obtained with aromatic compounds, but the stronger alkalinity of the aliphatic bases interferes with the end-point to some extent, and less accurate results are consequently obtained.

G. F. M.

**Preparation of Indigoid Dyes.** ADOLF JOLLES (D.R.-P. 305558; from *Chem. Zentr.*, 1919, iv, 619).—Aromatic hydroxyderivatives containing a phenolic hydroxyl group are oxidised in the presence of indoxyl or indoxyl acid. Thus a mixture of "2-naphthalene-2-indolindigo" and "4-naphthalene-2-indole-indolignone" (separable by extracting the latter with boiling dilute sodium hydroxide solution) is obtained when indoxyl and  $\alpha$ -naphthol dissolved in acetic acid are oxidised by a solution of ferric chloride in hydrochloric acid. A solution of the 20% indoxyl acid fusion and  $\alpha$ -anthrol, when similarly treated, yields "2-anthracene-2-indolindigo" (identical with the dye prepared from isatin- $\alpha$ -anilide and  $\alpha$ -anthrol).

H. W.

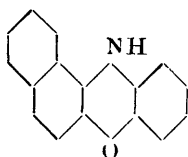
**Synthesis of 2:3-Pyridinoacenaphthene.** ALOIS ZINKE and EMMY RAITH (*Monatsh.*, 1919, 40, 271—276).—The experiments were undertaken with the object of ultimately preparing an  $\alpha$ -naphthaquinoline-6:7-dicarboxylic acid; the anhydride of such an acid is described, but the yields are not sufficiently satisfactory to permit further work.



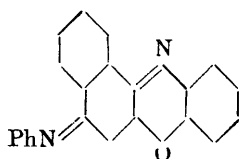
2:3-Pyridinoacenaphthene (annexed formula), colourless, ice-like crystals, m. p. 67° (uncorr.), is obtained by the action of concentrated sulphuric acid, glycerol, and nitrobenzene on 3-aminoacenaphthene. The hydrochloride, long, pale yellow needles, m. p. 305°, the sulphate, small, yellow needles, m. p. 238°, and the methiodide, yellow needles united in clusters, which does not melt below 315°, are described. Oxidation of the base or of its salts by chromic acid in acetic acid solution leads to the formation of  $\alpha$ -naphthaquinoline-6:7-dicarboxylic anhydride, long, red needles, m. p. 317°.

H. W.

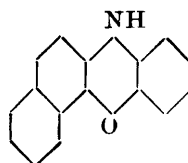
**1:2-Naphthaphenazoxines.** HENRI GOLDSTEIN and ZDENKA LUDWIG-SEMELITCH (*Helv. Chim. Acta*, 1919, **2**, 655—662. Compare Kehrman and Neil, A., 1915, i, 303).—1:2- $\alpha$ -Naphthaphenazoxine (annexed formula), yellow solid, m. p. 107° (decomp.), is prepared by gradually heating a mixture of  $\alpha$ -amino- $\beta$ -naphthol hydrochloride and *o*-aminophenol to 260° in a current of carbon dioxide; it is a very unstable substance which cannot be purified by crystallisation, the physical properties recorded being those of a small amount



of material which had sublimed during the preparation. The *acetyl* and *benzoyl* derivatives could not be obtained in the crystalline state. The composition of the substance is deduced from



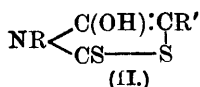
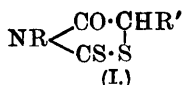
the conversion of the crude product into naphthaphenazoxone, on the one hand, and into 6-phenylnaphthaphenazoxime (annexed formula) on the other. The constitution of the latter substance is established by its synthesis from *o*-aminophenol hydrochloride and anilino- $\beta$ -naphthaquinone; it forms orange needles, m. p. 215°, and behaves as a very weak base. The *hydrochloride*, slender, red needles with green reflex, and the *platinichloride*, small, brown crystals, are described.



1:2- $\beta$ -Naphthaphenazoxine (annexed formula) is formed, together with the  $\alpha$ -isomeride, by heating a mixture of  $\alpha\beta$ -dihydroxynaphthalene and *o*-aminophenol. It forms yellow crystals, which darken in the air at about 110° and melt in a closed tube at 127—128°. The *acetyl* derivative could not be caused to crystallise. It is converted by aniline hydrochloride and ferric chloride into 3-phenylisonaphthaphenazoxime, which is a weak, unstable base; the *hydrochloride* and *platinichloride* are described.

H. W.

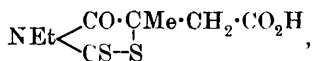
**Stereochemistry of Rhodanines. II.** STEN KALLENBERG (*Ber.*, 1919, **52**, [B], 2057—2071. Compare A., 1917, i, 279).—It is found that rhodanines with a tertiary  $\beta$ -carbon system and such as contain the asymmetric carbon atom outside the thiazole ring exhibit normal properties, and can be obtained in stable active forms. Rhodanines in which a hydrogen atom is united to the asymmetric  $\beta$ -carbon atom cannot be isolated in the active state. The most obvious explanation is to regard them as thiazolines (II) instead of thiazolidines (I), although it is also possible that a keto-enolic equilibrium is set up.



The condensation of *d*-thiolactic acid and phenylthiocarbimide

leads to the formation of *r*-3-phenyl-5-methylrhodanine, m. p. 114—116°.

*5-Methyl-3-ethylrhodanine-5-acetic acid*,



is prepared by the condensation of sodium *l*-methylbromosuccinate on potassium ethyldithiocarbamate in aqueous solution; it separates from water in long, pale yellow needles, m. p. 73—75° (+1H<sub>2</sub>O), 107—109° (anhydrous),  $[\alpha]_D - 54.4^\circ$  in alcoholic solution (for hydrated acid). The corresponding *d*-isomeride has m. p. 73—75°,  $[\alpha]_D + 55.5^\circ$ , and is optically stable towards barium hydroxide solution at the ordinary temperature. The *r*-acid forms thin, colourless, anhydrous leaflets, m. p. 108—110°.

It has been shown by Holmberg (A., 1912, i, 131) that trithiocarbodiglycollic acid condenses with *r*-β-phenylethylamine to yield 3-β-phenylethylrhodanine; if the action is carried out with the optically active bases, however, the active diphenylethylthiocarbamides, needles, m. p. 195—197°,  $[\alpha]_D - 13.5^\circ$  and  $+14.1^\circ$  in alcoholic solution, are produced, identical with the products described by Lovén and Ohlsson (A., 1914, i, 830). The active 3-phenylethylrhodanines may, however, be prepared as follows. *d*-Phenylethylamine is treated successively with aqueous potassium hydroxide solution and carbon disulphide and with an aqueous solution of sodium chloroacetate, whereby *d*-phenylethyldithiocarbamineglycollic acid, colourless, crystalline powder, m. p. 101—102°,  $[\alpha]_D + 120.4^\circ$  in alcoholic solution, is produced, which, when gently warmed with dilute acetic acid, loses water and passes into *d*-3-phenylethylrhodanine, pale yellow needles, m. p. 108—109°,  $[\alpha]_D + 301.2^\circ$  in alcoholic solution. *l*-Phenylethyldithiocarbamineglycollic acid has m. p. 101—102°,  $[\alpha]_D - 121.0^\circ$  in alcohol, whilst *l*-3-phenylethylrhodanine has m. p. 108—109°,  $[\alpha]_D - 304.8^\circ$ . The corresponding *r*-acid and *r*-rhodanine have m. p.'s 104—106° and 110—111° respectively. The latter is converted by a solution of sodium in alcohol into the substance,  $\text{CHMePh} \cdot \text{N} \begin{array}{l} \diagup \text{C}(\text{SH})(\text{OEt}) \\ \diagdown \text{CO} - \text{CH}_2 \end{array} \text{S}$ , small, pale red prisms, m. p. 93—94°, which could only be isolated in one of two possible stereoisomeric forms.

*r*-3-Ethylrhodanine-5-acetic acid, small, pale yellow needles, m. p. 118—119°, is obtained by the action of potassium ethyldithiocarbamate on sodium *l*-bromosuccinate in aqueous solution, racemisation being complete. The sodium hydrogen salt, greenish-yellow plates, m. p. 242—243° (decomp.), is described.

The possibility of obtaining optically active products from salts of *l*-bromosuccinic acid and dithiocarbamates is established by experiments with diethyldithiocarbamates; when the substances are allowed to react in dilute aqueous solution, *l*-diethyldithiocarbamine-malic acid,  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{S} \cdot \text{CS} \cdot \text{NEt}_2$ , m. p. 106—107°,  $[\alpha]_D - 6.67^\circ$  in alcohol,  $-40.9^\circ$  in ethyl acetate, is obtained, which is probably not optically pure and is completely racemised in boil-



ing aqueous solutions. When the condensation is effected in more concentrated solution, complete racemisation occurs, and the corresponding *r*-acid, m. p. 114—116°, is formed, which is also produced by the action of *r*-bromosuccinic acid on potassium diethyldithiocarbamate.

Sodium *l*- $\beta$ -bromosuccinamate condenses with potassium dimethyldithiocarbamate in aqueous solution to yield *l*-dimethyldithiocarbamylsuccinamic acid, colourless, silky needles, m. p. 158—159° (the sodium salt has  $[\alpha]_D - 4.2^\circ$  in aqueous solution), which, in hot acid solution, passes into *r*-dimethyldithiocarbamylsuccinic acid, small, rhombic plates, m. p. 145—146°, and in alkaline solution is extensively decomposed with formation of the half-amide of fumaric acid. The acid is oxidised by permanganate to *d*-dimethylthiocarbamylsuccinamic acid, m. p. 148—149°,  $[\alpha]_D + 80.5^\circ$  in alcoholic solution. *r*-Dimethyldithiocarbamylsuccinamic acid, small, colourless prisms, m. p. 162—163° (decomp.), is similarly prepared from *r*- $\beta$ -iodosuccinamic acid, and is similarly oxidised to *r*-dimethylthiocarbamylsuccinamic acid, colourless prisms, m. p. 153—154° (decomp.). A similar series of reactions yields *d*-phenylmethyldithiocarbamylsuccinamic acid, small, colourless prisms, m. p. 164—165° (decomp.),  $[\alpha]_D + 11.0^\circ$  in acetone (ammonium salt, colourless needles; sodium salt, small, colourless needles; potassium salt, colourless leaflets). The acid is converted into the *r*-ester, small, colourless, rhombic plates, m. p. 135—136°, by ethyl alcohol and hydrogen chloride. In hot acid solution it is transformed into *r*-phenylmethyldithiocarbamylsuccinic acid, m. p. 163—164°, and in alkaline solution it is extensively decomposed, yielding, amongst other products, the half-amide of fumaric acid. It is oxidised by permanganate to *d*-phenylmethylthiocarbamylsuccinamic acid, colourless, rhombic plates, m. p. 168° (decomp.),  $[\alpha]_D + 63.9^\circ$  in alcohol. *r*-Phenylmethyldithiocarbamylsuccinamic acid forms colourless, rhombic plates, m. p. 157—158° (decomp.), and is oxidised to *r*-phenylmethylthiocarbamylsuccinamic acid, prisms, m. p. 160—161° (decomp.).

H. W.

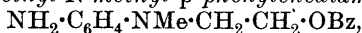
**3 : 3'-Dimethyl-6 : 6'-diisopropylbenzidine.** C. E. ANDREWS (U.S. Pat. 1314924).—Symmetrical dimethyldiisopropylbenzidine is produced by reducing crude mononitrocymene (such as may be obtained from "spruce turpentine") in alkaline solution to form hydrazocymene, subjecting the latter to the "benzidine transformation," and purifying the product by precipitation as sulphate. The sulphate is a white, crystalline powder which is easily separated by filtration, the impurities remaining in solution. The sulphate is decomposed on addition of a 10% sodium hydroxide solution, with liberation of the free base, dimethyldiisopropylbenzidine. The latter is an oily liquid, b. p. about 250°. It may be employed in the preparation of azo-dyes.

CHEMICAL ABSTRACTS.

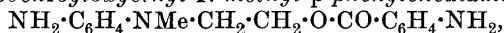
**Aromatic Analogues of Novocaine.** JULIUS VON BRAUN and GEORG KIRSCHBAUM (*Ber.*, 1919, 52, [B], 2011—2015).—It has

recently been shown by Fränkel and Cornelius (A., 1919, i, 66) that derivatives of primary  $\beta$ -aminoethyl alcohol, in contrast to the tertiary *N*-dialkylated alkamine derivatives (stovaine, novocaine), do not possess anæsthetising action. The compounds which they have examined, however, contain an acyl residue attached to the nitrogen atom in place of the alkyl radicle of novocaine, and thus do not belong to quite the same type. Closer analogy is shown by a series of substances, which are now described, and in which a phenyl or substituted phenyl group is introduced in place of one of the alkyl groups. It is found that the aromatic substitution at the nitrogen atom of novocaine is without influence on its anæsthetising power if the basicity of the molecule is also suitably increased.

*N*- $\beta$ -Benzoyloxyethyl-*N*-methyl-*p*-phenylenediamine,



long, slender needles, m. p.  $56^\circ$  (the *hydrochloride* and *acetyl* derivative, m. p.  $152^\circ$ , are described), is obtained by the reduction of the corresponding *p*-nitroso-derivative, pale green powder, m. p.  $90^\circ$ . Sodium *p*-nitrobenzoate reacts readily with  $\beta$ -chloro- or methyl- $\beta$ -bromo-ethyl-aniline, yielding *N*- $\beta$ -*p*-nitrobenzoyloxyethyl-*N*-methylaniline,  $\text{NMePh} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , yellow needles, m. p.  $70^\circ$  (*hydrochloride*, colourless substance, *picrate*, m. p.  $177^\circ$ , *methiodide*, m. p.  $144^\circ$  [decomp.]), which is reduced to *N*-*p*-aminobenzoyloxyethyl-*N*-methylaniline, colourless leaflets, m. p.  $112^\circ$  (*acetyl* derivative, m. p.  $132^\circ$ ). When the solution of the latter in dilute hydrochloric acid is treated with sodium nitrite, it yields the corresponding *p*-nitroso-derivative, m. p.  $105$ – $106^\circ$ , which is almost quantitatively reduced by stannous chloride to *N*- $\beta$ -*p*-aminobenzoyloxyethyl-*N*-methyl-*p*-phenylenediamine,

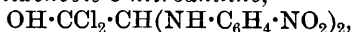


m. p.  $98^\circ$ ; the *hydrochloride* of the latter is freely soluble in water; the *diacetyl* derivative has m. p.  $146^\circ$ . Sodium 3:5-dinitrobenzoate and methylchloroethylaniline yield *N*- $\beta$ -3:5-dinitrobenzoyloxyethylmethylaniline, m. p.  $121^\circ$ , which is normally reduced to the corresponding *diamino*-compound, m. p.  $80^\circ$ , the *hydrochloride* of which is very hygroscopic.

H. W.

**Action of Basic Reagents on Schiff's Bases. I. The Chloralnitroaniline Group.** A. S. WHEELER and S. C. SMITH (*J. Amer. Chem. Soc.*, 1919, **41**, 1862–1865).—Schiff's bases, obtained by condensing *o*- and *p*-nitroaniline with chloral (compare Wheeler and Weller, A., 1903, i, 246), yield hydroxy-, methoxy-, and ethoxy-derivatives with alcoholic potassium hydroxide, sodium methoxide, and sodium ethoxide; in each case, one chlorine atom is replaced. The *m*-nitroaniline-chloral product is so sensitive to these basic reagents that each of them in the cold breaks it up into its constituents. The nitro-group in the benzene ring of the amine stabilises the Schiff's bases to such an extent that basic reagents yield derivatives, although this is not true when it is in the meta-position. The following new substances are described: NN'- $\beta\beta\beta$ -di-

*chlorohydroxyethylidenebis-o-nitroaniline*,



brilliant yellow prisms, m. p.  $143^\circ$ ; *NN'*- $\beta\beta\beta$ -*dichloromethoxyethylidenebis-o-nitroaniline*, yellow, rectangular plates, m. p.  $147^\circ$ ; *NN'*- $\beta\beta\beta$ -*dichloroethoxyethylidenebis-o-nitroaniline*, brilliant yellow, rectangular plates, m. p.  $135^\circ$ ; *NN'*- $\beta\beta\beta$ -*dichloroethoxyethylidenebis-p-nitroaniline*, bright yellow, fan-shaped crystals, m. p.  $147^\circ$ .

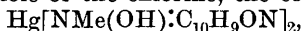
H. W.

**Constitution of Triphenylmethane Dyes.** HUGO KAUFFMANN (*Ber.*, 1919, **52**, [B], 1421—1422).—One of the most puzzling facts in connexion with the constitution of triphenylmethane dyes is the hypsochromic effect of the introduction of a third amino-group in such compounds as malachite-green (Hantzsch, A., 1919, ii, 255). This can only be explained on electrochemical lines, as developed by the author in his theory of valency subdivision (this vol., i, 50). A compound containing two methoxyl auxochromes in the third benzene nucleus of malachite-green has now been obtained by converting Michler's ketone into the chloride with phosphoryl chloride and condensing this with *m*-dimethoxybenzene under the influence of aluminium chloride. 4:4'-*Tetramethyldiamino-2''*:4''-*dimethoxytriphenylcarbinol* is white, has m. p.  $195^\circ$ , and dissolves in acids with the following colours: dilute acetic acid, bluish-green; dilute mineral acids, red becoming bluish-green on dilution; concentrated sulphuric acid, orange.

J. C. W.

### **The Incompatibility of Calomel and Antipyrine. I. A New Mercury Compound of Antipyrine.**

CESARE PADERI (*Arch. farm. speriment. sci. aff.*, 1918, **26**, 359—380; from *Chem. Zentr.*, 1919, iii, 226—227).—Poisonous symptoms are observed particularly in children to whom these substances have been administered simultaneously or after a certain interval, but nothing is definitely known with regard to the mode of action. The author has therefore investigated the mutual behaviour of these substances under various conditions. Reaction does not occur in the presence of water or of acid media, such as gastric juice. In the presence of alkalis, however, changes occur which cause a marked toxicity; the product is not mercuric chloride, but a metallo-organic compound, the composition of which depends on the relative quantities of alkali and calomel. If sufficient of the former is present to combine with the whole of the chlorine, the compound,



obtained by Astre and Ville by the action of mercuric oxide on antipyrine, is obtained; otherwise, a substance is produced which gives the reactions of antipyrine, but contains one atom of mercury and one of chlorine to each molecule of antipyrine, and to which the formula  $\text{HgCl} \cdot \text{NMe}(\text{OH}) \cdot \text{C}_{10}\text{H}_9\text{ON}$  is ascribed. Metallic mercury is also formed.

The new substance forms needles grouped in rosettes, m. p.  $92^\circ$ , and is sparingly soluble in cold water. It is more poisonous than

mercuric chloride. It gives precipitates with hydrogen sulphide or ammonium sulphide, and deposits mercury on copper; it does not react with sodium carbonate or potassium hydroxide, and only gives a slight precipitate with ammonia. With potassium ferrocyanide, it gives a flaky precipitate soluble in excess to a solution which slowly turns blue on exposure to air. Potassium iodide gives a turbid solution, from which a white precipitate, soluble in the warm or in excess of the reagent, slowly separates. A white precipitate is formed with stannous chloride, which disappears on shaking. Gold chloride gives a yellow precipitate, which is reduced when warmed. The substance also shows the antipyrine reactions with ferric chloride and with nitrous acid. H. W.

**Reaction of the Potassium Salts of 2-Thiol-5-thio-4-phenyl-4:5-dihydro-1:3:4-thiodiazole and 2:5-Dithiol-1:3:4-thiodiazole with Halogenated Organic Compounds.**

(SIR) PRAFULLA CHANDRA RÂY, PRAFULLA CHANDRA GUHA, and RADHA KISHEN DAS (T., 1919, 115, 1308—1312).

**Photochemical Transformations in the Triphenylmethane Series.** I. LIFSCHITZ [with CH. L. JOFFÉ] (*Ber.*, 1919, 52, [B], 1919—1926).—When triphenylmethane dyes are mixed with potassium cyanide, they change into colourless triarylacetonitriles (Hantzsch, A., 1900, i, 256; Müller, A., 1910, i, 868). It is now shown that these colourless nitriles are rearranged into the coloured triphenylmethane cyanides when exposed to the light of an iron arc in methyl- or ethyl-alcoholic solutions in quartz vessels, as, for example, in the *p*-rosaniline series,  $(\text{NH}_2 \cdot \text{C}_6\text{H}_4)_3\text{C} \cdot \text{CN} \rightarrow [(\text{NH}_2 \cdot \text{C}_6\text{H}_4)_3\text{C}] \text{CN}$ . Solvents like benzene, ether, and chloroform have no effect, because of their small dissociating power, but solutions in dilute mineral acids also remain colourless (provided that the nitrile is pure), the explanation in this case being that the selective absorption of the necessary long-wave ultra-violet light is prevented by the participation of the amino-groups in salt formation. Further evidence of the production of the ionisable salts is the fact that the electrical conductivity of the alcoholic solutions increases on exposing them to the light. The experimental evidence (absorption curves, etc.) is based on the cases of pararosaniline and crystal-violet. J. C. W.

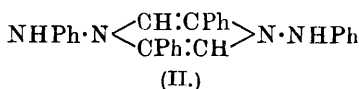
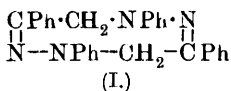
**Oxidation of the Hydramides.** J. BOUGAULT and P. ROBIN (*Compt. rend.*, 1919, 169, 978—980).—The three hydramides examined, benzhydramide, anishydramide, and piperonhydramide, on oxidation with iodine and sodium carbonate, all gave a 30—40% yield of the corresponding cyanidine. These cyanidines were subjected to hydrolysis with hydrochloric acid in acetic acid solution at a temperature not exceeding 120°. Under these conditions, triphenylcyanidine gave benzoic acid, ammonia, and benzamidine. Trimethoxyphenylecyanidine,  $(\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CN})_3$ , and trimethylene-

dioxyphenylcyanidine,  $(\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CN})_3$ , gave results of the same order.

Hydrocinnamide when oxidised by iodine and sodium carbonate did not give the corresponding cyanidine, but only an amorphous resin. The author considers that this result supports Delépine's view that hydrocinnamide is really a glyoxalidine. W. G.

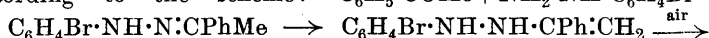
**Action of Hydrazines on  $\alpha$ -Chloro-ketones, and the Constitution of the so-called Tetraphenyltetracarbazone.**

SVEN BODFORSS (*Ber.*, 1919, **52**, [B], 1762—1775).—In 1886, Hess obtained a yellow compound, m. p.  $137^\circ$ , by the action of phenylhydrazine on  $\omega$ -bromoacetophenone in ice-cold alcohol, and assigned to it the formula  $\text{NPh} \begin{smallmatrix} \text{---} \text{N} \\ \text{CH}_2 \end{smallmatrix} \text{CPh}$ . This substance has been investigated by Culmann (A., 1890, 1268), who proposed a doubled formula,  $\text{C}_{28}\text{H}_{24}\text{N}_4$ , from very erroneous arguments, and the constitution of a tetraphenyltetracarbazone; Bender (A., 1888, 53, 1188); and Freer (A., 1899, 358); and recently Scholtz (A., 1918, i, 96), obtained a colourless compound, m. p.  $174^\circ$ , by condensing the agents in boiling alcohol, which he regarded as tetraphenyl- $\beta$ -tetracarbazone (I), that is, as an isomeride of Hess's compound. From an analogy with the action of ammonia on  $\omega$ -bromoacetophenone, which results in the formation of pyrazines (Tutin and Caton, T., 1910, **97**, 2495), it is more than likely that Scholtz's compound is 1:4-dianilino-2:5-diphenylpyrazine (II) or the -2:6-isomeride.

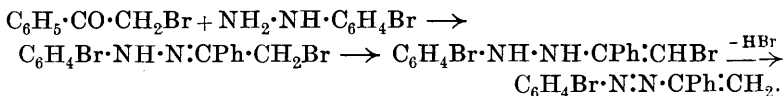


In order, in the first place, to get a correct idea of the molecular formula for Hess's compound, the author condensed  $\omega$ -*p*-dichloroacetophenone with phenylhydrazine under the same conditions, and obtained a product of the empirical formula  $\text{C}_{14}\text{H}_{11}\text{N}_2\text{Cl}$ . This confirms  $\text{C}_{14}\text{H}_{12}\text{N}_2$  as the simplest formula for Hess's compound, and as the molecular weight in boiling benzene is a little more than 200, this is also the molecular formula. Various alternative structural formulæ are critically examined, and arguments are advanced in favour of Hess's original suggestion. The substance should therefore be designated 1:3-diphenyl- $\Delta^2$ -1:2-diazene.

The product given by phenylhydrazine and  $\omega$ -*p*-dichloroacetophenone is, consequently, 1-phenyl-3-*p*-chlorophenyl- $\Delta^2$ -1:2-diazene,  $\text{NPh} \begin{smallmatrix} \text{---} \text{N} \\ \text{CH}_2 \end{smallmatrix} \text{C} \cdot \text{C}_6\text{H}_4\text{Cl}$ ; it crystallises in felted masses of thin, yellow needles, m. p.  $164\text{--}164.5^\circ$ .  $\omega$ -Bromoacetophenone and *p*-bromophenylhydrazine yield 3-phenyl-1-*p*-bromophenyl- $\Delta^2$ -1:2-diazene, orange, glistening needles, m. p.  $165^\circ$  (decomp.), that is, a substance quite distinct from Freer's azo-compound, formed according to the scheme:  $\text{C}_6\text{H}_5 \cdot \text{COMe} + \text{NH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Br} \rightarrow$

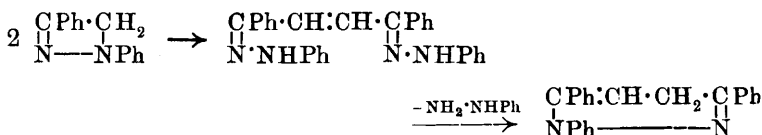


$C_6H_4Br \cdot N \cdot N \cdot CPh \cdot CH_2$ , with which it should be identical if Freer's interpretation of Hess's reaction is correct; thus,



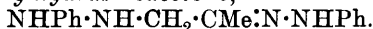
Phenylhydrazine and *p*-chloroacetylanisole yield 1-phenyl-3-*p*-anisyl- $\Delta^2$ -1:2-diazene, yellow, felted needles, m. p. 141° (decomp.).

When Hess's compound is treated with acids (best, alcoholic hydrogen chloride in the cold), it yields a compound,  $C_{22}H_{18}N_2$ , which Culmann regarded as a phenylhydrazine derivative of diphenacyl, since he obtained diphenacyl from it on boiling with 30% sulphuric acid. Freer, however, considered it to be the phenylhydrazone of deoxybenzoin. It is now found that Culmann was correct, for the compound (white needles, m. p. 114°) may be prepared by condensing diphenacyl with phenylhydrazine. The formation of this 1:3:6-*triphenyl*-1:4-*dihydropyridazine* from the diazene is explained in this way:



Phenylmethylhydrazine condenses with  $\omega$ -bromoacetophenone to form the phenylmethylosazone of phenylglyoxal, orange needles, m. p. 152° (Culmann). The same product is obtained by heating phenylmethylhydrazine with phenacylanilide, but in another *modification*, thin, orange-red, shimmering leaflets, m. p. 153—154°.

The reaction between chloroacetone and phenylhydrazine at low temperatures was described by Bender. The product is purified by crystallisation from methyl alcohol, whereby the m. p. is raised from 158° to 162·5°, and its properties suggest that it is the *phenylhydrazone* of *phenylhydrazinoacetone*,

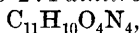


For example, it is oxidised by nitrous acid to methylglyoxalosotetrazone (von Pechmann, A., 1888, 1288). J. C. W.

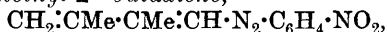
### The Coupling of Diazo-compounds with Hydrocarbons.

KURT H. MEYER (*Ber.*, 1919, 52, [B], 1468—1476).—In the majority of cases, the first step in the coupling of a compound with a diazonium salt is supposed by the author to be addition at double linkings (A., 1914, i, 882), but Karrer holds the opinion that addition at the amino-, hydroxy-, or alkyloxy-group represents the initial stage (A., 1915, i, 1073). It is now shown that certain unsaturated hydrocarbons can couple with suitable diazo-compounds, forming typical azo-derivatives, which indicates that, whilst Karrer's hypothesis may undoubtedly be correct in certain cases, addition at double bonds plays the principal rôle.

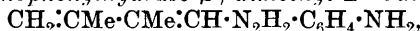
[With VIKTOR SCHOELLER.]—Butadiene couples with diazotised 2:4-dinitroaniline in glacial acetic acid to form  $\alpha$ -2:4-dinitrophenylazo- $\Delta^{\gamma}$ -butadiene,  $\text{CH}_2\text{:CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$ , in brilliant yellow needles, m. p.  $111^\circ$  (decomp.). Piperylene couples with the nitrobenzenediazonium chloride to form *p*-nitrophenylazopiperylene,  $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_3$ , glistening, yellow needles, m. p.  $137^\circ$ , and 2:4-dinitrophenylazopiperylene,  $\text{C}_{11}\text{H}_{10}\text{O}_4\text{N}_4$ , orange-yellow crystals, which darken at  $105^\circ$  and have m. p.  $131^\circ$  (decomp.). Isoprene forms 2:4-dinitrophenylazoisoprene,



orange-yellow crystals, m. p.  $98^\circ$  (decomp.). The best results are obtained with  $\beta\gamma$ -dimethyl- $\Delta^{\gamma}$ -butadiene, and it is rather suggestive that a methyl group in the  $\beta$ -position should have this favourable influence, for *m*-cresol methyl ether couples more readily than anisole (Auwers and Michaelis, A., 1914, i, 744).  $\alpha$ -*p*-Nitrophenylazo- $\beta\gamma$ -dimethyl- $\Delta^{\gamma}$ -butadiene,



forms long, yellow needles, m. p.  $177^\circ$ , gives an additive compound with mercuric chloride, brilliant red needles, decomp.  $109^\circ$ , a dark violet compound with stannic chloride, and a tetrabromide,  $\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}_3\text{Br}_4$ , dull orange, microscopic needles, m. p.  $132^\circ$  (decomp.), and may be reduced by means of tin and hydrochloric acid to  $\alpha$ -*p*-aminophenylhydrazo- $\beta\gamma$ -dimethyl- $\Delta^{\gamma}$ -butadiene,



a pale greenish-yellow base, m. p.  $125^\circ$  (decomp.), which is very easily oxidised on exposure to air.  $\alpha$ -2:4-Dinitrophenylazo- $\beta\gamma$ -dimethyl- $\Delta^{\gamma}$ -butadiene crystallises in bundles of slender prisms, decomp.  $126^\circ$ .

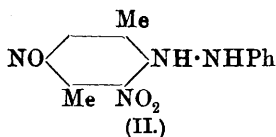
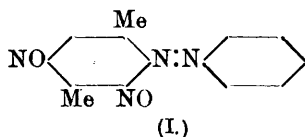
J. C. W.

**Aromatic Nitro-derivatives. VIII. Action of Phenylhydrazine on Trinitro-*p*-xylene and on Ethers of Trinitro-*m*-cresol.** M. GIUA (*Gazzetta*, 1919, 49, ii, 146—152. Compare A., 1918, i, 552).—Since trinitro-*p*-xylene contains a nitro-group which is readily replaceable, the action on it of phenylhydrazine should yield 3:5-dinitro-2-benzenehydrazo-*p*-xylene. Although formation of the latter in the first phase of the reaction may be assumed, it is found that the reaction proceeds further, reduction of a nitro-group and simultaneous elimination of a molecule of water from the  $\cdot\text{NH}\cdot\text{NH}\cdot$  group and another nitro-group in the ortho-position to it resulting in the formation of a 3:5-dinitroso-2-benzeneazo-*p*-xylene as final product; this is accompanied by 3-nitro-5-nitroso-2-benzenehydrazo-*p*-2-xylene, which represents an intermediate product.

The methyl and ethyl ethers of trinitro-*m*-cresol react in the same way as trinitroanisole (compare Giua and Cherchi, succeeding abstract) with phenylhydrazine, the alkyl-oxy-group being replaced by the phenylhydrazine residue, with formation of 3-benzenehydrazotrininitrotoluene. The latter is, however, so unstable that when heated to boiling with alcohol it is transformed immediately into 3-benzeneazonitrodinitrosotoluene; during this change, the alcohol is converted into aldehyde, the second nitro-

group in the ortho-position to the hydrazo-group being reduced and a molecule of water simultaneously eliminated from the hydrazo-group and the other nitro-group.

3:5-Dinitroso-2-benzeneazo-p-xylene (I) forms shining, yellow



plates, m. p. 185°, and yields a dark coloration when heated with potassium hydroxide in alcoholic solution.

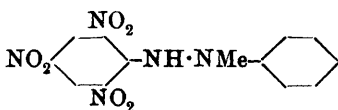
3-Nitro-5-nitroso-2-benzenehydrazo-p-xylene (II) forms shining, red, prismatic plates melting at 145° to a red oil, which readily decomposes if the heating is prolonged. With alkali and alcohol in the hot, it gives a deep red coloration, and when heated in presence of alcohol it is converted into the preceding compound.

6-Nitro-2:4-dinitroso-3-benzeneazotoluene (annexed formula) forms pale yellow, silky needles, m. p. 148—149°. Under the influence of light it becomes brownish-yellow, and with alkali in alcoholic solution it produces a reddish-brown coloration.

T. H. P.

**Aromatic Nitro-compounds. IX. Behaviour of Trinitroanisole.** M. GIUA and F. CHERCHI (*Gazzetta*, 1919, 49, ii, 152—157).—According to Masland and Sparre (*A.*, 1913, i, 853), trinitroanisole is hydrolysed, even in the cold, by solutions of alkali carbonates, with formation of picrates, and to some extent by water in the hot, with formation of methyl alcohol and picric acid, whilst cold water exerts only slight hydrolysing action. The authors regard this so-called hydrolysis as a process of substitution in the methoxy-group; this group is easily replaceable, even by radicles of organic bases, in consequence of the ortho-para-influence of the nitro-groups present in the molecule.

Trinitroanisole may be used with advantage to replace picryl chloride in many organic syntheses. Thus, with hydrazine hydrate it gives 2:4:6-trinitrophenylhydrazine; with phenylhydrazine, either trinitrohydrazobenzene or nitrodinitrosoazobenzene, according to the temperature, and with aniline, trinitrodiphenylamine, from which hexanitrodiphenylamine may be obtained by further nitration. The conditions necessary for all these reactions have been determined.



The action of *as*-phenylmethylhydrazine on trinitroanisole yields 2:4:6-trinitro-N<sup>1</sup>-methylhydrazobenzene (annexed formula), which crystallises in reddish-yellow or intense garnet-red prisms (probably

e\*



isomeric), m. p.  $153^{\circ}$ , and dissolves in concentrated sulphuric acid with a dark red coloration, and in alkali with a dark green coloration.

T. H. P.

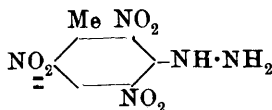
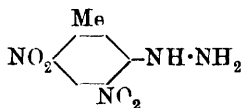
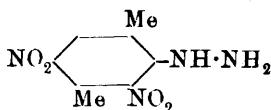
**Aromatic Nitro-derivatives. XI. Action of Hydrazine Hydrate on Aromatic Nitro-compounds.** M. GIUA (*Gazzetta*, 1919, **49**, ii, 166—175).—The action of hydrazine hydrate on various aromatic nitro-derivatives containing a labile nitro-group has been investigated. With trinitro-*p*-xylene and  $\beta$ - and  $\gamma$ -trinitrotoluenes, the reaction occurs readily in alcoholic solution, the labile nitro-group being replaced by the hydrazine residue. With the methyl ether of trinitro-*m*-cresol under the same conditions, the ortho-para-influence exerted by the nitro-groups on the methoxy-group brings about replacement of the latter by the hydrazine residue.

3:5-Dinitro-*p*-2-xylylhydrazine (annexed formula), prepared from trinitro-*p*-xylene and hydrazine hydrate, forms yellow prisms, m. p.  $180^{\circ}$  (decomp.), and with alkalis, in either alcoholic or acetone solution, gives a brick-red coloration. Its  $\beta$ -acetyl derivative,  $C_6HMe_2(NO_2)_2 \cdot NH \cdot NHAc$ , forms pale yellow, shining plates, m. p.  $232^{\circ}$  (decomp.), and gives a dark red coloration with alkalis in alcoholic solution. The  $\beta$ -benzylidene derivative,  $C_6HMe_2(NO_2)_2 \cdot NH \cdot N : CHPh$ , forms long, pale yellow needles, m. p.  $221^{\circ}$  (decomp.), and dissolves in potassium hydroxide to an intense violet-red solution. The  $\beta$ -anisylidene derivative,  $C_{16}H_{16}O_5N_4$ , crystallises in slender, golden-yellow needles, m. p.  $224^{\circ}$  (decomp.), and yields an intense carmine-red coloration with potassium hydroxide.

4:6-Dinitro-*m*-tolylhydrazine (annexed formula), prepared from  $\gamma$ -trinitrotoluene and hydrazine hydrate, forms reddish-yellow crystals, m. p.  $194^{\circ}$  (decomp.), its alcoholic solution being coloured intensely red by addition of an alkali.

The action of hydrazine hydrate on  $\beta$ -trinitrotoluene in alcoholic solution yields a compound which contains 28.31—28.7% N, and crystallises in golden-yellow prisms, m. p.  $150^{\circ}$  (decomp.); it may possibly be an aziminole derivative of the formula  $NO_2 \cdot C_6H_2Me \begin{smallmatrix} \text{N} \\ \text{N(OH)} \end{smallmatrix} \text{N}$ .

2:4:6-Trinitro-*m*-tolylhydrazine (annexed formula), prepared by the action of hydrazine hydrate on the methyl ether of trinitro-*m*-cresol (m. p.  $94^{\circ}$ ; Larter, P., 1901, 183, gave m. p.  $91^{\circ}$ ) (compare this vol., i, 19), crystallises in shining, golden-yellow plates, m. p.  $176^{\circ}$  (gas evolution), and dissolves in alkali solution, giving a brownish-red coloration. The  $\beta$ -acetyl



derivative,  $C_9H_9O_7N_5$ , forms large, yellow prisms, m. p.  $136^\circ$ , and gives a red coloration with alkali in alcoholic solution. The *αβ*-diacetyl derivative,  $C_6HMe(NO_2)_3 \cdot NAc \cdot NHAc$ , crystallises in nacreous plates, m. p.  $216^\circ$  (decomp.), and gives a dark red coloration with alkali in alcoholic solution. The *benzylidene* derivative,  $C_{14}H_{11}O_6N_5$ , forms small, reddish-yellow prisms, m. p.  $249-250^\circ$  (decomp.), burns with difficulty, leaving considerable carbonaceous residue, and dissolves in alkali solutions, giving an intense brick-red coloration.

T. H. P.

**The Proteolytic Activity of Pancreatic Amylase Preparations.** H. C. SHERMAN and DORA E. NEUN (*J. Amer. Chem. Soc.*, 1919, **41**, 1855—1862).—The experiments were undertaken with a view to throwing some further light on the nature of the relationship which exists between the amylolytic and proteolytic activities of purified pancreatic amylase preparations. High-grade commercial pancreatin was purified as described previously (Sherman and Schlesinger, A., 1912, i, 815; 1915, i, 604; Sherman and Neun, A., 1918, i, 414), except that in the final precipitation the usual 1:1 alcohol-ether mixture was replaced by a 2:1 mixture. A precipitate (*A*) is thus obtained, after removal of which a second precipitate (*B*) is isolated by adding more ether to the filtrate. The amylolytic activity of *A* is found to be lower than that of *B*, but the latter was more active than the usual amylase preparations; the proteolytic activity was higher in precipitate *A* than in precipitate *B*. Interpretation of the results is rendered difficult by the exceedingly unstable nature of the material under purification and the impossibility of pushing the fractionation further, because of the great tendency to loss of amylolytic activity when pancreatic amylase in the absence of salts and carbohydrates is held in solution or subjected to precipitation. On the whole, it seems probable that a partial separation of a mixture of amylase and protease was accomplished, but that amylolytic activity was partly lost because of the extra manipulation, since amylolytic activity deteriorates much more rapidly than proteolytic, at least under conditions such as obtained in these experiments. The further possibility that there are enzyme particles which have both amylolytic and proteolytic activities is not excluded. H. W.

**Influence of Aspartic Acid and Asparagine on the Enzymic Hydrolysis of Starch.** H. C. SHERMAN and FLORENCE WALKER (*J. Amer. Chem. Soc.*, 1919, **41**, 1866—1873. Compare Sherman, Walker, and Caldwell, A., 1919, i, 559).—The action of saliva, pancreatin, and purified pancreatic amylase on alkali-washed potato, wheat, maize, and rice starches, and on "Lintner" soluble starch, is accelerated by the addition of small amounts of boiled, neutralised water extract of potato, whilst the action of the vegetable amylases tested was not influenced by the addition of potato extract.

The addition of neutralised aspartic acid or asparagine accelerated

the action of saliva, pancreatin, and purified pancreatic and malt amylases. Clear evidence of activation was not obtained in the case of malt extract or of the preparations made from *Aspergillus oryzae*.

The addition of both sodium aspartate and asparagine to the same digestion mixture produces practically the same activation as does one of these substances alone. Thus the activating effects of the substances are interchangeable rather than additive. Activation is not due in these experiments to change in hydrogen-ion concentration or merely to a more favourable concentration of electrolyte. The amino-compounds to be tested were added to a substrate which already contained the optimum concentrations of sodium chloride and phosphate, the reported activation being thus additional to the activity induced by chloride and phosphate. Moreover, sodium aspartate is not interchangeable with sodium chloride in the activation of purified pancreatic amylase. The effects of other amino-acids are being studied similarly. H. W.

### **The Separation of Potato Tyrosinase into Components.**

HUGO HAEHN (*Ber.*, 1919, 52, [B], 2029—2041).—Potato tyrosinase can be separated by filtration into a thermolabile residue ( $\alpha$ -tyrosinase) and a filtrate (activator), which is stable towards heat; when separately tested, neither component shows the tyrosine reaction, but the mixture of the two is again active. The inactive residue can be activated by the addition of the solution obtained by boiling expressed potato juice in dilute acetic acid solution, and subsequent filtration, as also by the addition of an aqueous solution of the ash obtained by igniting the residue left on the evaporation of such a solution.

Toluene appears to act as an oxygen carrier; it is found that preservation of solutions beneath toluene does not inhibit the enzymic process of tyrosinase, as would be expected in consequence of the assumed exclusion of air. Further, it is shown that the alkaline solutions of pyrogallol become brown even when preserved beneath a layer of toluene which is 8 cm. high. The result is not due to hydroclastic activity of toluene, since the pyrogallol solutions remain unchanged when the experiment is performed in an atmosphere of hydrogen. H. W.

### **Urease and the Radiation Theory of Enzyme Action. III.**

H. P. BARENDRECHT (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 22, 29—45. Compare A., 1919, i, 604).—A continuation of previous work. From electrometric measurements of the hydrogen-ion concentration of phosphate solutions to which 8% of carbamide had been added, it is shown that the dissociation of water is decreased. The study of the urease action on carbamide was continued in solutions containing 5% of alcohol; all other conditions were the same as in the preceding experiments. It is shown that  $k_w$  is decreased from  $10^{-13.78}$  to  $10^{-13.98}$  by this addition, and the constant  $m$  for the hydrolysis of carbamide is reduced from 0.00381

to 0.00335. The influence of enzyme concentration is also studied. The results indicate that above a definite concentration of urease the activity is constant, but below this value the activity decreases.

J. F. S.

**Course of the Degradation of Urea by Urease.** H. VON EULER and G. BRANDTING (*Biochem. Zeitsch.*, 1919, **97**, 113—123).—Urease preparations previously kept at 17.5°, 30°, 35°, 40°, 45°, and 50° respectively for some days have shown constant activity. The authors cannot therefore confirm the periodicity in the activity of urease observed by Groll (A., 1919, i, 425). Groll's results are discussed.

S. S. Z.

**Biochemistry of the Enzyme of Soja Beans (Urease).** D. H. WESTER (*Chem. Weekblad*, 1919, **16**, 1442—1454).—A continuation of the author's previous research (A., 1916, ii, 502). The urease content of a solution, if not too dilute, may be estimated from the amount of urea which has undergone conversion. Neither the concentration of the urea solution nor the conversion products obtained affect the action of the enzyme. Urease solution retains its activity after prolonged storage, but it is necessary, on the other hand, to use freshly made urea solutions. For extracting the urease from the soja beans, glycerol to the extent of 50% may be added to the solution with advantage, but increased amounts will reduce the proportion of urease, and, further, the addition of glycerol to the mixture of urease and urea retards the enzymic process. The author finds that in some respects extract of *Canavalia* beans acts similarly to that of soja beans, but this investigation is still incomplete.

W. J. W.

**A Peculiarity of the Enzymic Action of Soja-bean Extract at 37°.** D. H. WESTER (*Chem. Weekblad*, 1919, **16**, 1461—1463).—Heating the extract for three days at 37° was found to reduce its efficiency, but heating for longer periods did not reduce the enzymic action proportionately. The following results were obtained:

Time .....	Hours.	Days.				
		7	14	21	28	35
Urea equivalent .....	126	47	38.2	90	85	60.3

The curve representing the above results is therefore a zigzag.

W. J. W.

**Action of Urease at 35°.** J. TEMMINCK GROLL (*Chem. Weekblad*, 1919, **16**, 1527).—The author confirms Wester's investigations (preceding abstract). He states that this behaviour is not a characteristic of one particular preparation, but is an actual property of urease and probably also of other ferments, such as lipases and ptyalin.

W. J. W.

**The Action of Neutral Salts on the Osmotic Pressure and other Qualities of Gelatin.** JACQUES LOEB (*Proc. Soc. Biol. Med.*, 1918, **15**, 129—131).—According to the author's hypothesis, neutral salts act on proteins, which, like gelatin, are stronger acids than bases, by forming metal proteinates. The anion either does not enter into combination at all with the gelatin or enters into a combination where its influence on the protein is not felt. When gelatin has been previously treated with an acid, for example, hydrochloric acid, gelatin chloride or hydrochloride is formed, which dissociates into a positive gelatin ion and a negative chlorine ion. Neutral salts act on such gelatin chloride by exchanging their anion for the protein. This explains why the increase in the osmotic pressure and the viscosity, and the swelling of gelatin caused by the salt, do not become noticeable unless the excess of salt is washed away, since the presence of the salt represses the electrolytic dissociation of the gelatin salt formed.

CHEMICAL ABSTRACTS.

**New Organic Compounds of Phosphorus.** H. STAUDINGER and JULES MEYER (*Helv. Chim. Acta*, 1919, **2**, 612—618).—Previous attempts to obtain a compound in which a nitrogen atom is directly united to five carbon atoms having proved unsuccessful (this vol., i, 34), the authors have turned their attention to the preparation of a similar compound from phosphorus, since, in general, this element shows a greater tendency to pass into the quinquevalent condition than does nitrogen.

Attempts to prepare phosphorus pentaethyl from tetraethylphosphonium iodide and zinc ethyl did not give the desired result, since action did not occur at low temperatures, whilst at 150° the products were butane and an additive product of triethylphosphine and zinc iodide. Triethylphosphine did not react with zinc ethyl or with magnesium ethyl bromide, whilst a phosphine-methylene derivative could not be prepared from triethylphosphine oxide and diphenylketen. The latter, however, unites readily with triethylphosphine (but not with triphenylphosphine) in absolute ethereal solution, yielding the unstable, pale yellow, crystalline additive product,  $\text{Et}_3\text{P} \begin{smallmatrix} \text{O} \\ \diagup \\ \text{C} \end{smallmatrix} \text{CPh}_2$ , which sinters at 80° and is completely decomposed at 100°. When heated, it dissociates into triethylphosphine and diphenylketen, and a similar phenomenon is observed when it is dissolved in benzene. It is decomposed by water into triethylphosphine and diphenylacetic acid.

Hofman has shown that triethylphosphine combines readily with carbon disulphide, and has formulated the product as a derivative of carbamide; since, however, it shows the closest analogy to the keten additive compound, the authors assign to it the structure

$\text{Et}_3\text{P} \begin{smallmatrix} \text{S} \\ \diagup \\ \text{C} \end{smallmatrix} \text{S}$ , which has previously been suggested by Jacobson (*Lehrbuch org. Chemie*, i, 427). When gently heated, it dissociates into carbon disulphide and triethylphosphine, whilst at a higher

temperature it yields triethylphosphine sulphide (the simultaneous formation of carbon monosulphide could not be established). The additive compound of triethylphosphine and phenylthiocarbimide is dissociated by gentle heating.

Carbodiphenyldi-imide does not react with triethylphosphine.

H. W.

**New Organic Compounds of Phosphorus. II. Phosphazines.** H. STAUDINGER and JULES MEYER (*Helv. Chim. Acta*, 1919, 2, 619—635).—Tertiary phosphines combine more or less readily with the most varied aliphatic diazo-compounds, yielding derivatives, for which the name phosphazines is proposed, in accordance with the scheme  $\text{CR}_2\text{:N:N} + \text{PR}_3 \rightarrow \text{R}_2\text{C:N:N:PR}_3$ . They are decomposed by water into the hydrazone and phosphine oxide. When heated, they lose nitrogen, but the exact course of the reaction has only been followed in the case of triphenylphosphinebenzophenoneazine, when triphenylphosphinediphenylmethylenes is produced (compare preceding abstract). They have more or less strongly marked basic properties and unite with two molecules of a monobasic acid to form salts, the constitution of which is not definitely established.

*Triethylphosphinefluorenoneazine*,  $\text{PEt}_3\text{:N:N:C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix}$ , golden-yellow, rather unstable crystals, m. p.  $160^\circ$ , is prepared by the action of diazofluorene on triethylphosphine in benzene solution in an atmosphere of nitrogen. With methyl iodide, it yields the product,  $\text{C}_{19}\text{H}_{23}\text{N}_3\text{P}\cdot\text{CH}_3\text{I}$ , pale yellow powder, m. p.  $109\text{--}113^\circ$ . It dissolves in dilute sulphuric and hydrochloric acids, and is recovered unchanged when the acid is neutralised; with the concentrated acids, it yields deep orange solutions, which become colourless on dilution with water. The yellow, crystalline *hydrochloride* is described. When hydrolysed with aqueous alcohol, it yields fluorenonehydrazine and triethylphosphine oxide, whilst with moist chloroform it yields *bisdiphenylenetetrahydrotetrazine* (?), orange-coloured crystals, m. p. about  $325^\circ$ .

*Triphenylphosphinefluorenoneazine* forms comparatively stable, compact, yellow crystals, m. p.  $209\text{--}210^\circ$  (decomp.). It is much more feebly basic than the triethylphosphine derivative, and neither unites with methyl iodide nor dissolves in dilute aqueous acids. The *hydrochloride* is an unstable substance which slowly loses hydrogen chloride when preserved; it softens at about  $193^\circ$ , but has not a definite m. p. *Phenyldiethylphosphinefluorenoneazine* is readily obtained in stable, yellow crystals, m. p.  $115^\circ$ , which are hydrolysed to fluorenonehydrazone and phenyldiethylphosphine oxide, and is feebly basic in character; the *hydrochloride*, pale yellow crystals, m. p. above  $250^\circ$  (indefinite), is described.

Diphenyldiazomethane reacts very readily with triethylphosphine, but the product, *triethylphosphinebenzophenoneazine*,



is so unstable that it could not be isolated in the pure state; its

formation is inferred from the fact that benzophenonehydrazine is obtained by the immediate treatment of the crude product with alcohol. When preserved, it readily yields *bisdiphenyltetrahydro-tetrazine*, pale yellow, crystalline powder, m. p. 204·5—205·5°. *Phenyldiethylphosphinebenzophenoneazine*,  $\text{PEt}_2\text{Ph}\cdot\text{N}\cdot\text{N}\cdot\text{CPh}_2$ , forms pale yellow crystals, m. p. 113°, and is hydrolysed to benzophenonehydrazone and phenyldiethylphosphine oxide. It dissolves in aqueous acids. *Triphenylphosphinebenzophenoneazine*,  $\text{PPh}_3\cdot\text{N}\cdot\text{N}\cdot\text{CPh}_2$ ,

is an almost colourless, stable, crystalline powder, m. p. 173° (decomp.). It is slowly hydrolysed to benzophenonehydrazone and triphenylphosphine oxide. It is scarcely affected by dilute acids. The colourless *hydrochloride* is a crystalline powder, m. p. ca. 185° (decomp.).

Triethylphosphine and phenyldiethylphosphine react with ethyl diazoacetate, but crystalline products could not be isolated; triphenylphosphine, on the other hand, yields *ethyl triphenylphosphineglyoxylate-azine*,  $\text{PPh}_3\cdot\text{N}\cdot\text{N}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , colourless crystals, m. p. 113—114°.

Benzoylphenyldiazomethane reacts readily with triethylphosphine and triphenylphosphine. Benzoyldiazoacetic ester also reacts with both phosphines, yielding azines, which will be described subsequently.

The tervalent phosphorus atom of phosphorus phenyl dichloride and of phosphorus trichloride appears unable to undergo these additive reactions.

H. W.

### New Organic Compounds of Phosphorus. III. Phosphinemethylene Derivatives and Phosphineimines. H.

STAUDINGER and JULES MEYER (*Helv. Chim. Acta*, 1919, 2, 635—646).—An account is given of the preparation and properties of two new classes of derivatives, namely, triphenylphosphinediphenylmethylenes, obtained by loss of nitrogen from triphenylphosphinebenzophenoneazine, as indicated in the preceding abstract, and phosphineimine compounds, produced by addition of azides to phosphines and spontaneous decomposition of the phosphazides primarily formed:  $\text{NPh}\cdot\text{N}\cdot\text{N} + \text{PPh}_3 \rightarrow \text{NPh}\cdot\text{N}\cdot\text{N}\cdot\text{PPh}_3 \rightarrow \text{NPh}\cdot\text{PPh}_3$ .

*Triphenylphosphinediphenylmethylenes*,  $\text{PPh}_3\cdot\text{CPh}_2$ , m. p. 170—172°, is best prepared by heating the corresponding azine in small quantities at a time in a vacuum at 185—195°. It crystallises from benzene in red leaflets, which contain approximately one molecule of benzene, which is only eliminated with difficulty. It dissolves in warm dilute hydrochloric acid, forming a colourless solution, from which *triphenylbenzhydrylphosphonium chloride*, colourless needles, m. p. 240—242°, separates on cooling. When heated with a solution of sulphur in carbon disulphide, it forms *t* iobenzophenone and triphenylphosphine sulphide. It does not react with carbon disulphide, benzylidenedianiline, dimethylaminobenzaldehyde, thiobenzophenone, or with diphenylketene. It

appears, therefore, to be considerably less reactive than diphenylketen, and its inability to unite with the latter is somewhat remarkable, more particularly since it is capable of reacting with phenylcarbimide to yield *diphenylketenphenylimine*.

*Triphenylphosphinephenylimine*,  $\text{PPh}_3\text{:NPh}$ , forms a pale yellow, crystalline powder or large plates, m. p.  $131\text{--}132^\circ$ , and is best prepared by the action of triphenylphosphine on phenylazide in absolute ethereal solution. It has feebly basic properties and dissolves to some extent in dilute sulphuric and hydrochloric acids; the boiling acids hydrolyse it to triphenylphosphine oxide and the aniline salt. It does not unite with substances containing a single double bond, such as benzaldehyde, benzylideneaniline, or thio-benzophenone. Reaction readily occurs, however, with compounds containing paired double linkings; thus, dry carbon dioxide at  $130\text{--}140^\circ$  converts it into triphenylphosphine oxide and phenylcarbimide, whilst triphenylphosphine sulphide and phenylthiocarbimide are formed with carbon disulphide. Triphenylphosphine oxide and triphenylphosphine sulphide are similarly obtained when it is gently warmed with phenylcarbimide and phenylthiocarbimide respectively. *Triphenylphosphine-p-tolylimine* forms pale yellow crystals, m. p.  $134\text{--}135^\circ$ , and is decomposed by carbon dioxide or carbon disulphide in the same manner as the phenylimine. *Triphenylphosphine-m-xylylimine* has m. p.  $130\text{--}131^\circ$ .

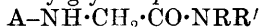
Phosphorus trichloride and phosphorus phenyl dichloride do not react with phenylazide.

Phenyldiethylphosphine and triethylphosphine in the undiluted condition react explosively with phenylazide. By conducting the action between the latter substances in the presence of absolute ether, it was found possible to isolate a crystalline *product*, golden-yellow leaflets, m. p.  $68\cdot5\text{--}69\cdot5^\circ$ , which was too unstable to permit further purification, but appears to have a nitrogen content higher even than that required for the phosphazide; triethylphosphine oxide was isolated from the ethereal mother liquor. H. W.

**Aromatic Arsenic Compounds. I. Plan of Procedure for the Synthesis of Arsenicals for Chemotherapeutic Research.** WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 1581—1587).—The general plan of a very comprehensive study of the chemotherapeutic value of arsenic compounds is developed. The authors consider that the salvarsan type of these substances has been fully investigated, and therefore turn their attention to products containing quinquevalent arsenic, using as starting point *p*-amino- or *p*-hydroxy-phenyl-arsinic acid or a similar derivative, and uniting this with an accessible group of simple type which is readily capable of chemical modification. They regard simplicity in chemical manipulation as a further essential to success. From these points of view, the following classes of compounds have been studied: diazoamino-compounds,  $\text{A-N:N-NRR}'$  (in which A is the arylarsinic radicle and R and R' hydrogen, alkyl, aryl, or substituted aryl groups),

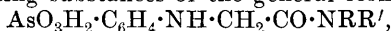


azo-dyes, A-N:N-R (in which R is the aromatic coupler), *N*-substituted amides of *N*-phenylglycine-*p*-arsinic acid,



(in which R and R' are hydrogen, alkyl, aryl, or substituted aryl groups),  $\beta$ -substituted carbamides of *N*-phenylglycine-*p*-arsinic acid, A-NH-CH<sub>2</sub>-CO-NH-CO-NHR, substituted *N*-phenylglycyl derivatives of arsanilic acid, A-NH-CO-CH<sub>2</sub>-NHR, substituted *o*-phenylglycine derivatives of arsanilic acid, A-NH-CO-CH<sub>2</sub>-OR, and substituted amides of *o*-phenylglycollic acid and *p*-arsinic acid, A-*o*-CH<sub>2</sub>-CO-NHR. Of these, the third type has up to the present yielded the most important results. H. W.

**Aromatic Arsenic Compounds. II. The Amides and Alkyl Amides of *N*-Arylglycinearsinic Acids.** WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 1587—1600. Compare preceding abstract).—The condensation of sodium arsanilate with chloroacetic acid to yield phenylglycine-*p*-arsinic acid has been described previously (D.R.-P. 204664); the authors now find that reaction occurs readily between sodium *p*-aminophenylarsinate and the amide and alkyl amides of chloroacetic acid, yielding substances of the general formula



in which R and R' may be hydrogen, alkyl, benzyl, or substituted benzyl radicles. The best experimental conditions consist in boiling aqueous solutions of sodium arsanilate and the simpler chloroacetyl alkylamines for a half to two hours; in the case of the chloroacetylbenzylamines, 50% alcohol is the most serviceable medium, and the addition of sodium iodide is found to be necessary.

All the glycineamidearsinic acids are colourless, crystalline substances which are generally sparingly soluble in the usual neutral media and possess high melting or decomposition points, the latter depending greatly on the rate of heating. They dissolve in alkali hydroxides or carbonates to form neutral salts, from which they are entirely displaced by acetic acid. They are more feebly basic than arsanilic acid itself, their hydrochlorides being stable only in the presence of concentrated hydrochloric acid. On boiling with excess of alkali or with mineral acids, the amide linking is hydrolysed, with the formation of glycinearsinic acid and the amine.

The following individual substances are described: *N*(phenyl-*p*-arsinic acid)-glycineamide (*N*-phenylglycineamide-*p*-arsinic acid), aggregates of long, thin plates, which darken and soften without melting at 280° when rapidly heated (the sodium salt [ $+\frac{1}{2}\text{H}_2\text{O}$ ] forms thin, nacreous plates readily soluble in water; the potassium and ammonium salts crystallise in thin, glistening, hexagonal, microscopic platelets; the calcium salt, microscopic, wedge-shaped prisms, is anhydrous; the magnesium salt forms a microcrystalline powder; heavy metal salts give immediate precipitates, the silver salt forming aggregates of thin, microscopic needles); *N*(phenyl-*p*-arsinic acid)-glycine methyl ester,  $\text{AsO}_3\text{H}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ ,

microscopic needles and thin plates, which soften and darken above  $200^{\circ}$  and decompose at about  $285^{\circ}$ ; the corresponding *ethyl* ester, delicate needles, m. p.  $270^{\circ}$  (decomp.); N(*phenyl-p-arsinic acid*)-nitrosoglycineamide,  $\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{NO}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$ , silky needles, decomposing at  $182$ — $183^{\circ}$ ; N(*phenyl-p-arsinic acid*)-glycinemethylamide, microscopic plates, which darken and soften above  $240^{\circ}$  and decompose at  $285^{\circ}$ ; N(*phenyl-p-arsinic acid*)-glycine-ethylamide, platelets, decomposing at  $278$ — $280^{\circ}$  after darkening above  $250^{\circ}$ ; N(*phenyl-p-arsinic acid*)-glycine-n-propylamide, microscopic needles, which do not melt below  $280^{\circ}$ ; N(*phenyl-p-arsinic acid*)-glycinedimethylamide, microscopic needles, decomposing at about  $241$ — $242^{\circ}$  when rapidly heated (the sodium salt,  $+4\text{H}_2\text{O}$ , is described); N(*phenyl-p-arsinic acid*)-glycinediethylamide, short needles, m. p.  $199$ — $201^{\circ}$  (decomp.) after softening and darkening above  $195^{\circ}$ ; N(*phenyl-p-arsinic acid*)-glycinepiperidide, microscopic needles, decomposing at  $218$ — $221^{\circ}$  after softening and darkening above  $200^{\circ}$ ; N(*phenyl-p-arsinic acid*)-glycinebenzylamide, microscopic needles, decomposing at  $282$ — $284^{\circ}$ ; N(*phenyl-p-arsinic acid*)-glycine-3'-carboxylamidobenzylamide,

$\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2$ , aggregates of microscopic needles, decomposing at  $237$ — $239^{\circ}$  with preliminary darkening (the sodium salt,  $+5\text{H}_2\text{O}$ , is described); N(*phenyl-p-arsinic acid*)-glycine-4'-acetylaminobenzylamide, diamond-shaped plates, which do not melt below  $280^{\circ}$  (the sodium salt forms microscopic needles,  $+4.5\text{H}_2\text{O}$ ); N(*phenyl-p-arsinic acid*)-glycine-3'-carboxylcarbamidobenzylamide,

$\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , delicate needles, decomposing at  $239$ — $240^{\circ}$ ; N(*phenyl-p-arsinic acid*)-glycine-4'-carbamidobenzylamide,

$\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ ; N(*phenyl-p-arsinic acid*)-glycine-3'-methyl-4'-acetylaminobenzylamide, flat needles, decomposing at  $278^{\circ}$  (the sodium salt,  $+6\text{H}_2\text{O}$ , is described); N(*phenyl-p-arsinic acid*)- $\alpha$ -aminopropionamide, thin, hexagonal plates, darkening above  $255^{\circ}$  and decomposing at  $262$ — $263.5^{\circ}$  (the sodium salt is described); *oxanilamide-p-arsinic acid*,  $\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CO} \cdot \text{NH}_2$ , minute needles, which do not melt or decompose below  $280^{\circ}$ .

N(*Phenyl-o-arsinic acid*)-glycineamide crystallises in thin plates which decompose at  $198$ — $199^{\circ}$ . N(*Phenyl-m-arsinic acid*)-glycineamide forms prismatic needles, m. p.  $175$ — $177^{\circ}$  (decomp.), whilst the corresponding methylamide crystallises in flat, microscopic needles or platelets, m. p.  $193$ — $194.5^{\circ}$  (decomp.).

The following derivatives of the aminotolylarsinic acids have been prepared: N(*o-tolyl-4-arsinic acid*)-glycineamide, delicate needles, which do not melt below  $285^{\circ}$ ; N(*o-tolyl-5-arsinic acid*)-glycineamide, glistening platelets, decomposing at about  $283^{\circ}$  after darkening above  $250^{\circ}$ ; N(*m-tolyl-6-arsinic acid*)-glycineamide, diamond-shaped platelets, m. p.  $203$ — $205^{\circ}$  (decomp.); N-*m-2-xylyl-5-arsinic acid glycineamide*, plates or prisms, m. p.  $236$ — $237^{\circ}$  (decomp.).

H. W.

### Aromatic Arsenic Compounds. III. The Carbamides and $\beta$ -Substituted Carbamides of *N*-Arylglycinearsinic Acids.

WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 1600—1610. Compare preceding abstracts).

—By replacing the amides of chloroacetic acid by carbamide and its alkyl or aryl derivatives in the reaction described in the previous paper, the carbamides and substituted carbamides of the arylglycinearsinic acids,



(where R may be hydrogen or an alkyl or aryl radicle), are obtained. The new series of substances closely resembles the amide series; they form stable and soluble neutral salts with the alkali metals. The carbamide linking, like that of the amides, is easily ruptured, this often occurring even at the ordinary temperature in solutions containing excess of alkali hydroxide. From the physiological point of view, the methylcarbamide of *N*-phenylglycine-*p*-arsinic acid is the most interesting member of the series. The following individual substances are described: *Derivatives of p-Arsanilic Acid*.—*N*(Phenyl-*p*-arsinic acid)-glycinecarbamide, microscopic needles, which darken, but do not melt, below 280° (the sodium salt [ $+2\text{H}_2\text{O}$ ], hexagonal platelets, the silver salt, microscopic needles, and the magnesium salt are described); *N*(phenyl-*p*-arsinic acid)-glycinemethylcarbamide, long, thin, glistening needles, decomposing at 224—225° (the sodium, silver, and magnesium salts were prepared); *N*(phenyl-*p*-arsinic acid)-glycine-ethylcarbamide, microscopic needles, decomposing at 223—225° (the sodium salt crystallises with  $4.5\text{H}_2\text{O}$ ); *N*(phenyl-*p*-arsinic acid)-glycinebenzylcarbamide, rosettes of needles, decomposing at 225°;  $\alpha$ -*N*(phenyl-*p*-arsinic acid)-aminopropionylcarbamide,  $\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , minute needles, which decompose at 225—226°; *N*(phenyl-*p*-arsinic acid)-glycine-phenylcarbamide, long, fine needles, which darken and melt at 280° (the sodium salt, flat needles [ $+5\text{H}_2\text{O}$ ], is described); *N*(phenyl-*p*-arsinic acid)-glycine-*p*'-acetylaminophenylcarbamide, flat, microscopic needles, decomposing at 265—266° after sintering and darkening above 240° (the sodium salt, flat needles [ $+5\text{H}_2\text{O}$ ], was prepared); *N*(phenyl-*p*-arsinic acid)-glycine-*m*'-oxamylaminophenylcarbamide,

$\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CO} \cdot \text{NH}_2$ , microcrystalline powder, decomposing at 223—224°; *N*(phenyl-*p*-arsinic acid)-glycine-*p*'-hydroxyphenylcarbamide, microscopic needles ( $+1.5\text{H}_2\text{O}$ ), not melting in the anhydrous state below 280° (the sodium salt is described); *N*(phenyl-*p*-arsinic acid)-glycyl-*p*'-carbamidophenoxyacetamide,

$\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$ , diamond-shaped platelets, decomposing at 243—244° after sintering and darkening (the sodium salt forms anhydrous plates); *N*(phenyl-*p*-arsinic acid)-glycyl-*m*'-carbamidobenzamide, flat, microscopic needles, m. p. 213—214° (decomp.); *N*(phenyl-*p*-arsinic acid)-glycyl-*p*'-carbamidobenzamide, decomposing at 245° after

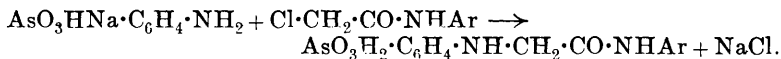
darkening above  $230^{\circ}$ ; *N*(phenyl-*p*-arsinic acid)-glycyl-*m*'-carbamidophenylacetamide, felted needles, which decompose at  $214\text{--}216^{\circ}$ ; *N*(phenyl-*p*-arsinic acid)-glycyl-*p*'-carbamidophenylacetamide, needles (+  $\text{H}_2\text{O}$ ), decomposing when anhydrous at  $218\text{--}221^{\circ}$  (the sodium salt forms microscopic, hexagonal platelets).

*Derivatives of o-Arsanilic Acid.*—*N*(Phenyl-*o*-arsinic acid)-glycinecarbamide, delicate needles, m. p.  $231\text{--}232^{\circ}$  (decomp.) when rapidly heated; *N*(phenyl-*o*-arsinic acid)-glycinemethylcarbamide, minute needles, m. p.  $218^{\circ}$  (decomp.).

*Derivatives of m-Arsanilic Acid.*—*N*(Phenyl-*m*-arsinic acid)-glycinecarbamide, colourless, microscopic needles, decomposing at  $208\text{--}209^{\circ}$ ; *N*(phenyl-*m*-arsinic acid)-glycinemethylcarbamide, m. p.  $213\text{--}213.5^{\circ}$  (decomp.).

*Derivatives of Substituted Arsanilic Acids.*—*N*(*m*-Tolyl-6-arsinic acid)-glycinecarbamide, delicate needles, decomposing at about  $235^{\circ}$  (the sodium salt forms glistening plates +  $2\text{H}_2\text{O}$ ); *N*(*m*-tolyl-6-arsinic acid)-glycinemethylcarbamide, hair-like needles, decomposing at  $218\text{--}219^{\circ}$ ; *N*(2-hydroxyphenyl-5-arsinic acid)-glycinecarbamide, flat, glistening needles (+  $1\text{--}1.5\text{H}_2\text{O}$ ), decomposing when anhydrous at  $203\text{--}205^{\circ}$ .  
H. W.

**Aromatic Arsenic Compounds. IV. Aromatic Amides of *N*-Arylglycinearsinic Acids.** WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 1610—1644. Compare preceding abstracts).—An extensive series of compounds has been prepared in accordance with the general scheme:



In the cases of the more reactive chloroacetyl derivatives, reaction may be effected in boiling aqueous solution, but with the more stable compounds, 50% alcohol is a more suitable solvent, and sodium iodide should be added. In general, it is found that *m*-arsanilic acid condenses more readily than the ortho- or para-isomerides. The compounds have generally weakly basic and acidic functions; the free arsenic acids do not, as a rule, possess sharp melting or decomposition points, the values obtained depending greatly on the rate of heating. They are, on the whole, but sparingly soluble in the usual media. The sodium salts, on the other hand, dissolve more or less readily in water, and were prepared for convenience in biological testing, and also as a convenient means of purification of the compounds. The following individual substances are described.

*Derivatives of p-Arsanilic Acid.*—*N*(Phenyl-*p*-arsinic acid)-glycineanilide,  $\text{AsO}_3\text{H}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$ , minute, delicate needles, which do not melt below  $285^{\circ}$  (the sodium salt, glistening scales [+  $4\text{H}_2\text{O}$ ], and the nitroso-compound, flat, colourless needles [+  $\text{H}_2\text{O}$ ], decomposing at  $190\text{--}192^{\circ}$ , are described); *N*(phenyl-*p*-arsinic acid)-glycine-*o*'-toluidide, needles, which are not decomposed

below  $275^{\circ}$  (*sodium* salt, long, narrow platelets [ $+2.5\text{H}_2\text{O}$ ]); N(*phenyl-p-arsinic acid*)-*glycine-m'-toluidide*, long, thin plates decomposing at  $285^{\circ}$ ; N(*phenyl-p-arsinic acid*)-*glycine-p'-toluidide*, woolly masses of minute needles, which do not decompose below  $280^{\circ}$  (*sodium* salt, thin, curved, glistening needles  $+3\text{H}_2\text{O}$ ); N(*phenyl-p-arsinic acid*)-*glycine- $\alpha$ -naphthylamide*, microscopic needles, which darken, but do not melt, below  $280^{\circ}$ ; N(*phenyl-p-arsinic acid*)-*glycine- $\beta$ -naphthylamide*, microscopic needles, decomposing at  $285$ — $286^{\circ}$  to a red liquid (*sodium* salt, flat needles  $+4.5\text{H}_2\text{O}$ ); N(*phenyl-p-arsinic acid*)-*glycinediphenylamide*, long, thin, microscopic leaflets ( $+ \text{H}_2\text{O}$ ), decomposing when anhydrous at  $271$ — $272^{\circ}$ ; N(*phenyl-p-arsinic acid*)-*glycine-p'-chloroanilide*, toothed, microscopic leaflets, which do not melt below  $280^{\circ}$ ; N(*phenyl-p-arsinic acid*)-*glycine-p'-iodoanilide*, broad, minute needles, which do not melt below  $275^{\circ}$  (*sodium* salt, needles  $+3.5\text{H}_2\text{O}$ ); N(*phenyl-p-arsinic acid*)-*glycine-p'-nitroanilide*, thin, faintly yellow needles, not melting below  $285^{\circ}$ ; N(*phenyl-p-arsinic acid*)-*glycine-p'-acetylaminoanilide*, microscopic needles, which do not melt below  $285^{\circ}$  (*sodium* salt, minute, lustrous platelets); N(*phenyl-p-arsinic acid*)-*glycine-p'-aminoanilide* (by hydrolysis of the acetyl derivative or reduction of the corresponding nitro-compound), colourless, microscopic needles or platelets, decomposing at  $253$ — $254^{\circ}$ ; N(*phenyl-p-arsinic acid*)-*glycine-p'-carbamidoanilide*, pale brown, microcrystalline aggregates ( $+0.5\text{H}_2\text{O}$ ), decomposing when anhydrous at  $230^{\circ}$  after darkening above  $200^{\circ}$  (*sodium* salt, microscopic needles  $+4\text{H}_2\text{O}$ ); N(*phenyl-p-arsinic acid*)-*glycine-4'-methyl-5'-carbamidoanilide*, microscopic platelets and hairs, decomposing at  $257$ — $258^{\circ}$  (*sodium* salt, crystalline powder  $+3.5\text{H}_2\text{O}$ ); N(*phenyl-p-arsinic acid*)-*glycine-m'-oxamylaminoanilide*,

$\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CO} \cdot \text{NH}_2$ , microcrystalline aggregates, which darken and partly decompose, but do not melt below  $280^{\circ}$ ; N(*phenyl-p-arsinic acid*)-*glycyl-o'-aminophenol*, lustrous crystals, m. p.  $190^{\circ}$  (decomp.) after preliminary darkening; N(*phenyl-p-arsinic acid*)-*glycine-m'-hydroxyanilide*, which is of special importance, owing to its reduction to arsenophenylglycinebis-m'-hydroxyanilide; N(*phenyl-p-arsinic acid*)-*glycine-4-hydroxy-o-toluidide*, pink plates or prisms, decomposing at about  $220$ — $225^{\circ}$ ; N(*phenyl-p-arsinic acid*)-*glycine-2'-hydroxy-p-toluidide*, prisms, m. p.  $258^{\circ}$  (decomp.); N(*phenyl-p-arsinic acid*)-*glycine-p'-hydroxyanilide*, glistening platelets, m. p.  $255$ — $260^{\circ}$  (decomp.) (*sodium* salt, lustrous leaflets  $+4.5\text{H}_2\text{O}$ ); N(*phenyl-p-arsinic acid*)-*glycine-p'-anisidide*, lustrous leaflets, which darken and soften above  $230^{\circ}$ ; N(*phenyl-p-arsinic acid*)-*glycine-1-hydroxy- $\beta$ -naphthalide*, microscopic plates and prisms ( $+2\text{H}_2\text{O}$ ), decomposing, when anhydrous, at  $189$ — $191^{\circ}$ ; N(*phenyl-p-arsinic acid*)-*glycine-4-hydroxy- $\alpha$ -naphthalide*, microscopic crystals, decomposing, when anhydrous, at  $240$ — $242^{\circ}$  after darkening above  $200^{\circ}$  (*sodium* salt, glistening plates  $+5.5\text{H}_2\text{O}$ ); N(*phenyl-p-arsinic acid*)-*glycyl-4:6-dichloro-3-hydroxyanilide*, flat, colourless, microscopic needles, m. p. about  $280^{\circ}$  (decomp.) after darkening above  $200^{\circ}$ ; N(*phenyl-p-arsinic*

acid)-glycyl-6-bromo-3-hydroxyanilide, glistening leaflets, decomposing at  $255^{\circ}$ ; N(phenyl-p-arsinic acid)-glycine-3':4'-dihydroxyanilide, glistening leaflets, decomposing at about  $260$ — $265^{\circ}$  after blackening above  $200^{\circ}$ ; N(phenyl-p-arsinic acid)-glycylanthranyl acid, octahedra, which decompose at  $230$ — $235^{\circ}$  (the corresponding ethyl ester forms needles which do not decompose below  $280^{\circ}$ ); N(phenyl-p-arsinic acid)-glycyl-N-methylanthranyl acid, microscopic aggregates of needles or plates, decomposing at  $230^{\circ}$ ; N(phenyl-p-arsinic acid)-glycyl-2'-aminobenzamide, microscopic needles ( $+H_2O$ ), m. p.  $170^{\circ}$  (sodium salt, minute crystals  $+4.5H_2O$ ); N(phenyl-p-arsinic acid)-glycyl-m'-aminobenzamide, irregular, microscopic platelets, which are not completely decomposed below  $280^{\circ}$ ; N(phenyl-p-arsinic acid)-glycyl-m'-aminobenzoyl-carbamide, microscopic needles, decomposing at about  $280^{\circ}$  (sodium salt, microscopic hairs  $+8H_2O$ ); N(phenyl-p-arsinic acid)-glycyl-p'-aminobenzamide, microscopic needles, which do not melt below  $280^{\circ}$  (sodium salt, thin, microscopic needles  $+4.5H_2O$ ); N(phenyl-p-arsinic acid)-glycyl-5'-aminosalicylamide, glistening scales ( $+H_2O$ ), which, when anhydrous, softens above  $190^{\circ}$  and gradually decomposes until fluid at about  $255^{\circ}$ ; N(phenyl-p-arsinic acid)-glycyl-m'-aminophenylacetamide, microscopic needles, decomposing at  $275$ — $280^{\circ}$  after darkening above  $220^{\circ}$ ; N(phenyl-p-arsinic acid)-glycyl-p'-aminophenylacetic acid, microscopic globules, m. p.  $280^{\circ}$  (decomp.); N(phenyl-p-arsinic acid)-glycyl-p'-aminophenylacetamide, microscopic hairs, which do not decompose below  $280^{\circ}$  (sodium salt, glistening platelets  $+4.5H_2O$ ); N(phenyl-p-arsinic acid)-glycyl-p'-aminophenylacetylcarbamide, minute hairs, which do not melt below  $280^{\circ}$  (sodium salt, minute, hexagonal plates  $+3H_2O$ ); N(phenyl-p-arsinic acid)-glycyl-o'-aminophenoxyacetamide, minute needles, decomposing at about  $280^{\circ}$  with preliminary darkening; N(phenyl-p-arsinic acid)-glycyl-m'-aminophenoxyacetic acid, decomposing at about  $250$ — $260^{\circ}$  after softening at  $180$ — $190^{\circ}$ ; N(phenyl-p-arsinic acid)-glycyl-p'-aminophenoxyacetic acid, flat, microscopic needles or platelets, which do not melt below  $285^{\circ}$  (sodium salt, glistening leaflets  $+3H_2O$ ); N(phenyl-p-arsinic acid)-glycyl-p'-aminophenoxyacetamide, flat needles, which do not melt below  $280^{\circ}$  (sodium salt, microscopic needles  $+5H_2O$ ); N(phenyl-p-arsinic acid)-glycyl-p'-aminophenoxyacetylcarbamide, microscopic needles, slowly decomposing at  $290^{\circ}$  (sodium salt, microscopic needles  $+4H_2O$ ); N(phenyl-p-arsinic acid)-glycyl-3-methyl-4-aminophenoxyacetic acid, microscopic needles, decomposing at  $270^{\circ}$  (sodium salt, well-defined needles); N(phenyl-p-arsinic acid)-glycyl-m'-aminobenzenesulphonamide, flat, glistening needles, which decompose at about  $265^{\circ}$  with preliminary darkening; N(phenyl-p-arsinic acid)-glycyl-p'-aminobenzenesulphonic acid, flat needles ( $+2H_2O$ ), slowly decomposing when anhydrous, at  $245$ — $246^{\circ}$ ; N(phenyl-p-arsinic acid)-glycyl-p'-aminobenzenesulphonamide, thin, microscopic leaflets and needles, which do not melt below  $280^{\circ}$ ; N(phenyl-p-arsinic acid)-glycyl-4-amino-6-hydroxybenzenesulphonic acid, microscopic leaflets ( $+1.5H_2O$ ), which, when anhydrous, softens and darkens above

200°, but does not melt below 275°; N(*phenyl-p-arsinic acid*)-glycyl-4-aminoacetophenone, long, fine hairs, which do not melt below 280°.

*Derivatives of o-Arsanilic Acid.*—N(*Phenyl-o-arsinic acid*)-glycineanilide, minute prisms (+1H<sub>2</sub>O), melting with decomposition at 160—163° when anhydrous; N(*phenyl-o-arsinic acid*)-glycine-*o*'-hydroxyanilide, glistening needles (+0.5H<sub>2</sub>O), m. p. (anhydrous) 151—153° (decomp.); N(*phenyl-o-arsinic acid*)-glycine-*m*'-hydroxyanilide, pink, microscopic platelets (+2H<sub>2</sub>O), m. p. 103—105°, m. p. of anhydrous substance about 180° (decomp.) after softening at about 125—130°; N(*phenyl-o-arsinic acid*)-glycine-*p*'-hydroxyanilide, colourless, microscopic platelets, m. p. 208—209° (decomp.).

*Derivatives of m-Arsanilic Acid.*—N(*Phenyl-m-arsinic acid*)-glycineanilide, prisms, decomposing at 217—218°; N(*phenyl-m-arsinic acid*)-glycine-*o*'-hydroxyanilide, flat, microscopic needles, m. p. 190—192° (decomp.) (the ammonium salt forms minute needles); N(*phenyl-m-arsinic acid*)-glycine-*m*'-hydroxyanilide, minute, irregular platelets and flat needles (+1.5H<sub>2</sub>O), decomposing, when anhydrous, at about 180—190°; N(*phenyl-m-arsinic acid*)-glycine-*p*'-hydroxyanilide, microscopic platelets, which slowly decompose at 180°.

*Derivatives of Substituted and p-Arsanilic Acids.*—N(*o-Tolyl-5-arsinic acid*)-glycine-*m*'-hydroxyanilide, long, flat, microscopic needles, which slowly darken and decompose at 285°; N(*o-tolyl-5-arsinic acid*)-glycine-*p*'-hydroxyanilide, spindle-shaped needles, decomposing at 232—233° with preliminary darkening; N(*m-tolyl-6-arsinic acid*)-glycine-*m*'-hydroxyanilide, spindle-shaped microcrystals, which decompose at 232—235° after softening and darkening; N(*2-carboxyphenyl-4-arsinic acid*)-glycine-*m*'-hydroxyanilide, minute platelets (+1H<sub>2</sub>O), decomposing, when anhydrous, at 204—207° after darkening and swelling. H. W.

**Aromatic Arsenic Compounds. V. *N*-Substituted Glycyl-arsanilic Acids.** WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 1809—1821. Compare preceding abstracts).—The substances under discussion are closely related to the previously described substituted anilides of phenylglycine-*p*-arsinic acid, but differ from these in the fact that the glycine side-chain is reversed, the arsenic radicle becoming a substituent on the anilide nucleus. The substances are readily prepared by boiling the sodium salt of chloroacetylarsanilic acid with the aromatic amino-compound in aqueous solution. The substituted phenylglycylarsanilic acids closely resemble the isomeric anilides of phenylglycine-*p*-arsinic acid, functioning both as acids and feeble bases. They are but sparingly soluble in the usual media, and all have high melting or decomposition points, the observed values depending on the rate of heating. In general, the sodium salts are readily soluble in water. The following individual substances have been prepared.

Chloroacetyl-*p*-arsanilic acid,  $\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$  (compare D.R.-P. 191548), conveniently prepared by heating dry chloroacetic acid with *p*-arsanilic acid on the water-bath, minute, lenticular platelets and toothed leaflets, m. p.  $285^\circ$  (decomp.); *glycyl-p*-arsanilic acid, glistening plates, which do not melt below  $295^\circ$  (*iminobisacetyl-p*-arsanilic acid, micro-crystals, darkening without melting at  $280$ — $285^\circ$ , is formed as by-product of the action of aqueous ammonia on chloroacetyl-*p*-arsanilic acid); *N*-methylglycyl-*p*-arsanilic acid, silky, glistening needles ( $+2\text{H}_2\text{O}$ ), which darken at about  $250^\circ$ , but do not melt below  $275^\circ$ ; *N*-phenylglycyl-*p*-arsanilic acid, felted needles, which do not melt below  $280^\circ$ ; *m*-oxaminophenylglycyl-*p*-arsanilic acid,

$\text{CO}_2\text{H} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}_3\text{H}_2$ , decomposing, when anhydrous, at  $179^\circ$ , hydrated acid  $+1\text{H}_2\text{O}$  (the hydrochloride is described); *p*-aminophenylglycyl-*p*-arsanilic acid, microcrystalline aggregates, which darken and soften, but do not melt, below  $280^\circ$ ; *p*-acetaminophenylglycyl-*p*-arsanilic acid, hexagonal platelets, not melting below  $275^\circ$  (the sodium salt forms flat, glistening needles  $+7\text{H}_2\text{O}$ ); *p*-oxaminophenylglycyl-*p*-arsanilic acid, microscopic crystals  $+1.5\text{H}_2\text{O}$ , darkening in the anhydrous state above  $200^\circ$ , but not melting below  $275^\circ$ ; *p*-oxamylaminophenylglycyl-*p*-arsanilic acid, microscopic needles, not melting below  $285^\circ$  (the sodium salt was prepared); *p*-carbamidophenylglycyl-*p*-arsanilic acid, microscopic leaflets, which do not melt below  $285^\circ$ ; *m*-hydroxyphenylglycyl-*p*-arsanilic acid, prisms  $+3.5\text{H}_2\text{O}$ , which melt in their water of crystallisation at about  $80^\circ$  (the hydrochloride is described); *p*-hydroxyphenylglycyl-*p*-arsanilic acid, microscopic hairs ( $+1\text{H}_2\text{O}$ ), which, when anhydrous, blacken and sinter above  $200^\circ$ , but do not melt entirely below  $280^\circ$  (the sodium salt, aggregates of microscopic needles  $+ \text{H}_2\text{O}$ , was prepared); *m*-carboxylamidophenylglycyl-*p*-arsanilic acid, microscopic needles, decomposing at  $248^\circ$  (sodium salt, radiating masses of flat needles  $+1\text{H}_2\text{O}$ ); *N*-phenylglycineanilide-*m*-carboxycarbamide-*p*'-arsinic acid,

$\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , microscopic needles, decomposing at about  $280^\circ$  (sodium salt, flat, microscopic needles  $+3\text{H}_2\text{O}$ ); *p*-carboxylamidophenylglycyl-*p*-arsanilic acid, microscopic prisms, which do not melt below  $275^\circ$  (sodium salt, glistening platelets  $+2\text{H}_2\text{O}$ ); *N*-phenylglycineanilide-*p*-acetamide-*p*'-arsinic acid,

$\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$ , microscopic platelets, decomposing at  $256$ — $258^\circ$  after darkening and softening above  $180^\circ$ ; *N*-phenylglycineanilide-*p*-acetylcarbamide-*p*'-arsinic acid, microscopic hairs  $+0.5\text{H}_2\text{O}$ , which decompose, when anhydrous, at  $270$ — $273^\circ$  after darkening above  $230^\circ$ ; *N*-phenylglycineanilide-*p*-oxyacetic-*p*'-arsinic acid,

$\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , minute, wedge-shaped plates  $+1.5\text{H}_2\text{O}$ , decomposing in the anhydrous state at about  $275^\circ$  after darkening above  $180^\circ$ ; *N*-phenylglycineanilide-*p*-oxyacetamide-*p*'-arsinic acid, woolly needles not melting below  $265^\circ$  (sodium salt, rosettes of flat, glistening needles  $+4\text{H}_2\text{O}$ ); *N*-phenylglycineanilide-*p*-oxyacetocarb-

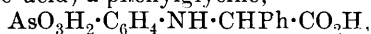


*amide-p'-arsinic acid*, minute platelets, which decompose at 257—258° with preliminary darkening (*sodium salt*, minute leaflets + 4H<sub>2</sub>O); *N-phenylglycineanilide-p-glycineamide-p'-arsinic acid*, micro-crystals (+1.5H<sub>2</sub>O), which, when anhydrous, do not melt below 285°; *N-phenylglycineanilide-4:4'-diarsinic acid*,

AsO<sub>3</sub>H<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH·CH<sub>2</sub>·CO·NH·C<sub>6</sub>H<sub>4</sub>·AsO<sub>3</sub>H<sub>2</sub>, microscopic needles (+0.5H<sub>2</sub>O), not melting below 280° when anhydrous; *p-acetylphenylglycyl-p-arsanilic acid*, microscopic needles, which darken and decompose when heated, but do not melt below 290° (*sodium salt*, pale yellow, glistening platelets + 3H<sub>2</sub>O).

H. W.

**Aromatic Arsenic Compounds. VI. *N*-(Phenyl-*p*-arsinic acid)- $\alpha$ -phenylglycine and its Amides.** WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 1822—1825. Compare preceding abstracts).—As a special extension of the general type of substances represented by the substituted amides, carbamides, and anilides of the phenylglycinearsinic acids. *N*(phenyl-*p*-arsinic acid)- $\alpha$ -phenylglycine,



its amide, carbamide, and certain substituted anilides have been prepared. With the exception of the glycine itself, which was obtained by hydrolysis of the amide, the substances were made from sodium arsanilate and the phenylchloroacetyl-amino-compounds. It was found necessary to use sodium iodide and 50% alcoholic solution. The general properties of this group of substances are similar to those of the simpler glycine derivatives.

The following compounds are described: *N*(phenyl-*p*-arsinic acid)- $\alpha$ -phenylglycine, lustrous, rhombic plates, decomposing at 202—203° after darkening and softening; *N*(phenyl-*p*-arsinic acid)- $\alpha$ -phenylglycineamide, microscopic needles, which do not melt below 280° (*sodium salt*, granular aggregates of plates + 3.5 to 5H<sub>2</sub>O); *N*(phenyl-*p*-arsinic acid)- $\alpha$ -phenylglycinecarbamide, microscopic needles + 1H<sub>2</sub>O, decomposing when anhydrous at 195—197°; *N*(phenyl-*p*-arsinic acid)- $\alpha$ -phenylglycine-3'-hydroxyanilide, lenticular platelets + 1.5H<sub>2</sub>O, decomposing at 155—160°: the anhydrous substance has m. p. about 200—210° (decomp.), after softening at about 155—160°; *N*(phenyl-*p*-arsinic acid)- $\alpha$ -phenylglycine-4'-carbamidoanilide, decomposing at about 255° with preliminary darkening and softening; *N*(phenyl-*p*-arsinic acid)- $\alpha$ -phenylglycine-3'-carbamidoanilide, microcrystalline powder, m. p. 261—262° (decomp.); *N*(phenyl-*p*-arsinic acid)- $\alpha$ -phenylglycyl-4-aminophenylacetamide, AsO<sub>3</sub>H<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH·CHPh·CO·NH·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CO·NH<sub>2</sub>, minute plates and flat needles + 0.5H<sub>2</sub>O, melting in the anhydrous condition at 222—223° (decomp.).

H. W.

**Aromatic Arsenic Compounds. VII. Substituted Benzyl-, Phenoxyethyl- and Phenacyl-arsanilic Acids.** WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 1826—1833. Compare preceding abstracts).—It has been

shown previously that the reactivity of the amino-group in arsanilic acid with chloroacetyl-amino-compounds is such as to render possible the synthesis of a very extensive series of aromatic arsinic acids. The authors now describe a preliminary series of experiments with other aromatic derivatives containing suitable alkyl haloid side-chains. Thus benzyl and substituted benzyl chlorides react with sodium arsanilate under suitable conditions to form benzyl- and substituted benzyl-arsanilic acids, reaction proceeding readily with negatively substituted benzyl chlorides. Similarly, the required derivatives are slowly formed from phenoxyethyl bromide and allied substances, whilst with phenacyl haloids the reaction also proceeds in the desired sense.

The following individuals are described: *benzyl-p-arsanilic acid*, arborescent masses of micro-crystals and larger prisms, decomposing at about  $255^{\circ}$  (sodium salt, glistening platelets); *p-nitrobenzyl-arsanilic acid*, yellow, microscopic needles, which do not melt below  $280^{\circ}$ ; *p-aminobenzylarsanilic acid* (by reduction of the *p*-nitro-acid with ferrous hydroxide), microscopic leaflets, decomposing at about  $202^{\circ}$ ; *3-nitro-4-hydroxybenzylarsanilic acid*, minute, yellow crystals ( $+1\text{H}_2\text{O}$ ), decomposing when anhydrous at about  $245\text{--}250^{\circ}$  after darkening and sintering above  $210^{\circ}$  (sodium salt, thin, yellow, microscopic needles); *3-amino-4-hydroxybenzylarsanilic acid*, microscopic platelets ( $+0.5\text{H}_2\text{O}$ ), which do not melt below  $285^{\circ}$  when anhydrous; *p-carboxybenzylarsanilic acid*, microscopic needles which do not melt below  $280^{\circ}$  (sodium salt, microcrystalline powder  $+0.5\text{H}_2\text{O}$ ); *p-carboxylamidobenzylarsanilic acid*, microscopic needles, not melting below  $280^{\circ}$  (sodium salt, thin plates  $+2.5\text{H}_2\text{O}$ ).

*Phenoxyethylarsanilic acid*,  $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$ , glistening scales ( $+1\text{H}_2\text{O}$ ), which, when anhydrous, do not melt below  $280^{\circ}$  (sodium salt, flat, microscopic needles  $+3.5\text{H}_2\text{O}$ ); *p-acetylaminophenoxyethylarsanilic acid*, thin, narrow plates which do not melt below  $275^{\circ}$  (sodium salt, colourless, microscopic platelets  $+3\text{H}_2\text{O}$ ); *o-carboxylamidophenoxyethylarsanilic acid*, broad, microscopic needles not melting below  $280^{\circ}$ ; *phenacylarsanilic acid*,  $\text{COPh}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$ , faintly yellow aggregates of delicate, microscopic needles, which decompose at  $185\text{--}187^{\circ}$ ; *2-hydroxy-5-acetylaminophenacylarsanilic acid*, microscopic platelets, decomposing at  $228^{\circ}$ . [*3-Acetyl-amino-6-hydroxyphenacyl bromide*, from acetophenetidide, bromoacetyl chloride, and aluminium chloride, forms a drab-coloured powder, m. p.  $133\text{--}135^{\circ}$  (slight decomp.).] H. W.

**Aromatic Arsenic Compounds. VIII. The Amides of (*p*-Arsinic Acid)-phenoxyacetic Acid and the Isomeric Phenoxyacetylarsanilic Acids.** WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 1834—1840. Compare preceding abstracts).—Chloroacetyl-amino-compounds react with sodium *p*-hydroxyphenylarsinate (compare D.R.-P. 216270) to yield arsinic acids which crystallise readily when pure, have high decomposition points, are sparingly soluble in the usual media, and are more strongly acidic than the amides of phenylglycinearsinic acid. The success of the condensation depends on the addition of

an extra molecule of sodium hydroxide in order to form the sodium phenoxide, and this condition depresses the yield in the cases in which the haloid contains a labile halogen atom. Similarly, the sodium salt of chloroacetylarsanilic acid reacts with phenols to yield phenoxyacetyl or phenyl ether glycolylarsanilic acids, which are more strongly acidic than the glycolarsanilic acids. On reduction, both of these groups of substances yield arsenoxides and arseno-compounds which will be more fully described in a later communication.

The following substances have been prepared: *methyl (p-arsinic acid)-phenoxyacetate*,  $\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$ , lustrous plates, which partly melt at about  $192-195^\circ$  (decomp.); (*p-arsinic acid*)-*phenoxyacetamide*, rhombic, microscopic prisms, which do not melt below  $280^\circ$  (*sodium salt*, glistening platelets); (*p-arsinic acid*)-*phenoxyacetanilide*, minute prisms and microscopic plates, which darken slightly above  $250^\circ$ , but do not melt below  $280^\circ$ ; (*p-arsinic acid*)-*phenoxyaceto-m-hydroxyanilide*, sandy powder, m. p.  $238-240^\circ$  (decomp.) (*sodium salt*, lustrous, microscopic needles and long, thin platelets); (*p-arsinic acid*)-*phenoxyaceto-p-hydroxyanilide*, curved, colourless, microscopic crystals, decomposing at  $238-240^\circ$  (the *sodium salt* and (?) nitroso-compound were prepared); (*p-arsinic acid*)-*phenoxyacetyl-4-aminophenylcarbamide*, microscopic needles, which darken and soften at about  $230-240^\circ$ , but do not melt entirely up to  $265^\circ$ .

*Phenoxyacetylarsanilic acid*,  $\text{OPh} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}_3\text{H}_2$ , colourless crystals which darken slightly above  $250^\circ$ , but do not decompose below  $280^\circ$ ; *p-oxaminophenoxyacetylarsanilic acid*, cream-coloured crystals, which darken but do not melt below  $280^\circ$  (a hydrated form  $+1\text{H}_2\text{O}$  is also described); *p-carbamidophenoxyacetylarsanilic acid*, microscopic spindles, decomposing at about  $280-283^\circ$  with preliminary darkening (*sodium salt*, minute needles  $+3\text{H}_2\text{O}$ ); *o-carboxylamidophenoxyacetylarsanilic acid*, delicate needles which do not decompose below  $280^\circ$  (*sodium salt*, prismatic needles  $+5.5\text{H}_2\text{O}$ ); *p-carboxylamidophenoxyacetylarsanilic acid*, long, glistening needles, not melting below  $280^\circ$  (*sodium salt*, long, flat needles,  $+7.5\text{H}_2\text{O}$ ).  
H. W.

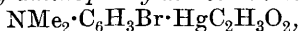
**Action of Arsenic Acid on Polyhydric Phenols.** ADOLF SONN (*Ber.*, 1919, 52, [B], 1704).—The polyhydric phenols suffer oxidation when heated with arsenic acid in the usual way, but if pyrogallol and dilute arsenic acid solutions are concentrated in a vacuum and left in the cold, a crystalline *pyrogallol arsenate*,  $\text{AsO}[\text{O} \cdot \text{C}_6\text{H}_3(\text{OH})_2]_3$ , is deposited.  
J. C. W.

**1:3-Benzodiazolearsinic Acids and their Reduction Products.** ROBERT REGINALD BAXTER and ROBERT GEORGE FARGHER (*T.*, 1919, 115, 1372—1380).

**Organic Mercury Compounds Derived from *p*-Bromodimethylaniline.** FRANK C. WHITMORE (*J. Amer. Chem. Soc.*, 1919, 41, 1841—1854).—The paper is the first of a series in which the introduction of mercury in the ortho-position to various substi-

tuted amino-groups will be studied. The reactions involved may be represented by the single equilibrium equation,  $R_2Hg + HgX_2 \rightleftharpoons 2RHgX$ , in which R represents any organic residue which has its free bond attached to carbon and X represents any univalent acid radicle. The reaction normally runs to completion to the right because of the slight solubility of the organo-mercuric salt,  $RHgX$ , in the organic solvents used. It may, however, be reversed by using reagents which remove  $HgX_2$ , such as alkaline reducing agents and compounds like potassium iodide and sodium thiosulphate, which form mercuric complexes of considerable stability.

*5-Bromo-2-dimethylaminophenylmercuriacetate,*



colourless needles, m. p.  $144^\circ$ , is prepared by the action of mercuric acetate on *p*-bromodimethylaniline in cool, aqueous alcoholic solution in 74% yield; simultaneously, smaller quantities of mercurous acetate and of a tar are produced. Formation of the latter is more pronounced in warm, concentrated solution; it can be suppressed to some extent by gradually adding the mercuric acetate to the well-agitated solution, but the yield of the mercury derivative also suffers. The mercury is not precipitated by hydrogen sulphide. The corresponding *chloride*, very fine needles, m. p.  $183^\circ$ , *bromide*, m. p.  $182^\circ$ , *iodide*, m. p.  $169^\circ$ , and *thiocyanate*, white, gritty crystals, m. p.  $135^\circ$ , decomposing at  $140^\circ$ , were obtained by the action of alcoholic solutions of the acetate on alcoholic solutions of calcium chloride, sodium bromide, potassium iodide, and potassium thiocyanate respectively. *5-Bromo-2-dimethylaminophenylmercurihydroxide*, from the acetate and sodium hydroxide in alcoholic solution, forms hard, nodular masses of crystals, m. p.  $162^\circ$ , and evolves gas without blackening at  $165^\circ$ . The *formate*, from the hydroxide and ethyl formate, crystallises in fine, felted needles, m. p.  $145^\circ$ , and decomposes at  $150^\circ$ .

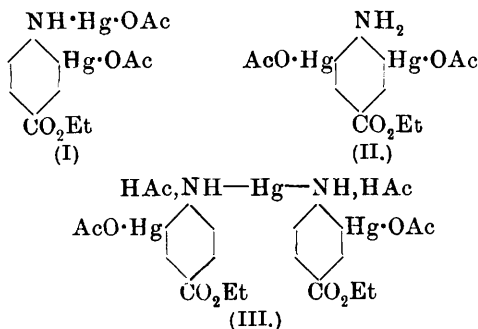
*Mercury di-5-bromo-2-dimethylaminophenyl*, colourless needles, m. p.  $123^\circ$ , is most conveniently prepared (86% yield) by boiling a solution of the acetate in alcohol with potassium iodide, but the formation of *p*-bromodimethylaniline could not be suppressed completely. Reaction appears to depend on the formation of a stable iodine complex,  $M_2HgX_4$ , and evidence in support of this hypothesis is afforded by experiments with sodium or ammonium bromide or calcium chloride. The complexes formed by bromine and chlorine are less stable than those formed by iodine, and the yield of the mercury diphenyl compound drops to 3% with the bromides and to zero with the chloride. Conversion of the acetate into the mercury diphenyl derivative is less advantageously effected with sodium stannite solution (yield, 63%), and only very unsatisfactorily with sodium thiosulphate or potassium sulphide; with the latter reagent the *sulphide* was isolated as hard, white flakes which become grey at about  $97^\circ$  and partly melted at  $115$ – $120^\circ$ . The formate, when heated for a protracted period in benzene alcoholic solution, yielded mainly mercury and *p*-bromodimethylaniline and a small quantity of the mercury diphenyl compound. Reduction of the acetate by

zinc dust in boiling alcoholic solution gave mercury, unchanged acetate, and *p*-bromodimethylaniline; with copper powder under similar conditions very little reaction occurred.

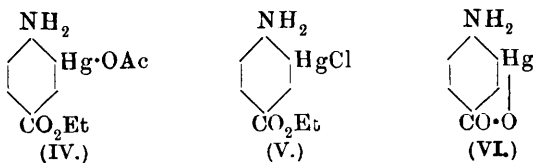
The mercury diphenyl derivative is quantitatively transformed into 5-bromo-2-dimethylaminophenylmercurichloride when heated with mercuric chloride in the presence of alcohol; the bromide, iodide, and thiocyanate may be obtained similarly and in good yield, but the iodide obtained in this manner is not nearly so pure as the corresponding bromide or chloride. When the mercury diphenyl derivative is heated in an analogous manner with mercuric sulphate, it yields basic mercuric sulphate and *p*-bromodimethylaniline.

H. W.

**The Doctrine of Substitution. II. Mercuration of Ethyl *p*-Aminobenzoate.** WALTER SCHOELLER, WALTER SCHRAUTH and ERWIN LIESE (*Ber.*, 1919, **52**, [B], 1777—1787. Compare A., 1914, i, 892).—When ethyl *p*-aminobenzoate is left with mercuric acetate in cold methyl alcohol, a pale yellow precipitate of *ethyl N*:3-diacetoxydimercuri-4-aminobenzoate (I), m. p. 245°, is slowly deposited.



This is converted into *ethyl 3:5-diacetoxydimercuri-4-aminobenzoate* (II), a felted mass of long needles, m. p. 255—257°, on warming with glacial acetic acid, this being formed directly if acetic acid is used as the solvent in the first condensation. In a mixture of methyl alcohol and acetic acid, however, the white, microcrystalline substance (III), m. p. 230—240°, is produced. This is resolved into compound (I) and *ethyl 3-acetoxymercuri-4-aminobenzoate* (IV) (bundles of white needles, m. p. 182°, and again at 228°) on boiling with methyl alcohol, and into compounds (II) and (IV) on warming with glacial acetic acid. Compound (IV) is best obtained by melting the original agents together, when at 160° the mass solidifies again



and the desired product may be extracted by hot methyl alcohol. Compounds (I) and (IV) react with sodium chloride in a mixture of methyl alcohol and acetic acid to form *ethyl 3-chloromercuri-4-aminobenzoate* (V), which crystallises in small, white prisms, m. p. 223°, but compound (II) differs from compound (I) in forming *ethyl 3:5-dichlorodimercuri-4-aminobenzoate*, small needles, m. p. 270°, under these conditions. When boiled with dilute sodium hydroxide, compound (IV) loses the ester and acetyl groups, and the sodium salt so formed deposits flocculent, white *3-hydroxymercuri-4-aminobenzoic anhydride* (VI) on acidification.

As a proof that the amino-group is free in compound (II), which is a type not produced in the case of anthranilic acid, the formation of its *acetyl* derivative (small needles, m. p. 247°) is advanced.

J. C. W.

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## Physiological Chemistry.

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**The Absence of the Bromine Reaction for Tryptophan in Tryptically Digested Leucocytes.** MORITZ WEISS (*Biochem. Zeitsch.*, 1919, **98**, 116—120).—Tryptically digested leucocytes do not give the bromine reaction for tryptophan. Putrified pus shows the presence of indole, but only traces of indole derivatives can be demonstrated in it by the uorosein reaction (hydrochloric acid and sodium nitrite). The pus cells give a strong Adamkiewicz-Liebermann reaction. Whilst casein manifests a blue coloration, leucocytes give a violet coloration in this reaction. It is concluded that a derivative of tryptophan, but not tryptophan itself, is concerned in the synthesis of leucocytes. S. S. Z.

**Origin of Odour.** H. TEUDT (*Deutsch. Essigind.*, 1919, **23**, 160—162; from *Chem. Zentr.*, 1919, iii, 239).—The author has been able to develop his theory further by a consideration of the atomic models of Rutherford and Bohr, and has deduced the causes which are operative in setting the valency electrons within the molecule into such vibrations as produce odour (compare A., 1919, i, 607). The original paper must be consulted for details. H. W.

**The Chromium Reaction of Certain Tissues as an Adrenaline Reaction.** W. STOELTZNER (*Münch. med. Woch.*, 1919, **66**, 584; from *Chem. Zentr.*, 1919, iii, 60).—It has not been observed previously that adrenaline gives the same reaction with chromic acid as certain tissues. A dilute, pale yellow solution of potassium dichromate becomes intensely brown after addition of adrenaline, and gradually deposits a brown precipitate. The shade exactly matches the brown coloration assumed by the tissue when treated with dichromate, and the chromium reaction of the tissue must therefore be due to adrenaline. H. W.

**Presence of Hæmatoporphyrin in the Urine and Fæces of a Case of Acute Hæmatoporphyrinuria.** WILHELM LÖFFLER (*Biochem. Zeitsch.*, 1919, **98**, 105—116).—The coloured urine of a patient suffering from Landry's disease was examined for hæmatoporphyrin. The urine was precipitated with glacial acetic acid and the precipitate dissolved in potassium hydroxide. After reprecipitating and redissolving in *N*/10-potassium hydroxide, the fraction showed the typical spectrum of hæmatoporphyrin. A portion of the hæmatoporphyrin was methylated by H. Fischer's method. The compound thus obtained melted at 262° (not sharp), and gave the same spectrum as Fischer's preparation. The hydrolysed methyl ester yielded the original hæmatoporphyrin.

0.2 Gram of hæmatoporphyrin was excreted in twenty-four hours. On extracting the fæces of the same patient by Fischer's bicarbonate method and with methyl alcohol and hydrochloric acid the presence of small quantities of hæmatoporphyrin similar to that extracted by Fischer from a similar source was established.

S. S. Z.

**The Action of Strophanthin on Colloids.** GEORG PIETRKOWSKI (*Biochem. Zeitsch.*, 1919, **98**, 92—104).—The action of strophanthin on optically invisible colloidal gold solutions produces an increase in the number of particles visible under the ultra-microscope. In the case of an hydrophile colloid, such as gelatin, strophanthin inhibits imbibition. These facts, it is suggested, justify the conclusion that the increase in tonus in the cardiac muscles brought about by the action of this drug is due to the shrinking of the surface of the muscle fibres. The above experiments, however, do not explain the specificity of strophanthin.

S. S. Z.

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## Chemistry of Vegetable Physiology and Agriculture

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**Butylene Glycol Fermentation of Sucrose by Bacteria of the Prodigiosus Group.** M. LEMOIGNE (*Compt. rend. soc. biol.*, 1919, **82**, 234—236; from *Chem. Zentr.*, 1919, iii, 198).—In addition to acid and traces of ethyl alcohol and acetaldehyde,  $\beta\gamma$ -butylene glycol and acetylmethylcarbinol are invariably found among the products of the decomposition of sucrose by different varieties of *B. prodigiosus*. The bacteria, therefore, ferment sucrose in the same manner as those of the group of *B. subtilis*, *B. lactis aerogenes*, and *Staphylococci* (A., 1913, i, 1422). H. W.

**The Alkali-forming Bacteria found in Milk.** S. HENRY AYERS, PHILIP RUPP, and WILLIAM T. JOHNSON, jun. (*U.S. Dept. of Agriculture*, 1919, Bull. No. 782).—The group of bacteria

studied is defined as consisting of those which produce an alkaline reaction in milk without peptonisation of the casein. This group produced the reaction in five days at 30°. The reaction was not due to ammonia, as ammonia was produced by a few organisms only, and then not until the second week. All the citric acid in the milk was used up, and an amount of carbonate corresponding with about half the citric acid was produced. The chief sources of these organisms were milk, soil, and water. Of the species studied, six were cocci and sixty-two were bacilli; all were non-sporing, and had an optimum temperature of 20—30°.

The action of each organism on certain organic compounds was examined, using cultivations in a sodium ammonium phosphate medium containing the test substance as the only source of carbon. The change in the hydrogen-ion concentration was taken as the measure of the alkalinity produced. It was found that dextrose and galactose were fermented by forty-four cultures, lactose by eleven, saccharose by two, and raffinose by none. Ethyl, propyl, and amyl alcohols were more readily fermented than mannitol and glycerol. The sodium salts of many organic acids were also used, with the result that pyruvic, citric, malic, lactic, succinic, acetic, propionic, butyric, valeric, hexoic, mucic, glyceric, tartaric, malonic, formic, benzoic, and salicylic acids were converted into carbonates, and oxalic and glycollic acids were unacted on. *n*-Butyric, *n*-valeric, and *n*-hexoic acids were first converted into simpler acids. An investigation of the results showed that the organisms took their carbon most readily from the alkyl and primary alcohol groups, provided the primary alcohol was not linked to a carboxyl group. A secondary alcohol group was less easily acted on than a primary. The carboxyl group was not split up. Some experiments were made with urea, uric acid, and hippuric acid, as sources of both carbon and nitrogen, and most of the organisms grew well in these media, as also did the well-known organisms of typhoid, paratyphoid, and dysentery. All the organisms were able to utilise the nitrogen in nitrates and nitrites.

J. H. J.

**Transformation of Cyanamide into Carbamide by the Microbes of the Soil.** P. MAZÉ, VILA, and M. LEMOIGNE (*Compt. rend.*, 1919, **169**, 921—923).—It is shown that numerous common species of bacteria abundant in all soils in a good state of cultivation can grow in the presence of cyanamide at a concentration of 1 in 1000, and are capable of rapidly converting the cyanamide into carbamide.

W. G.

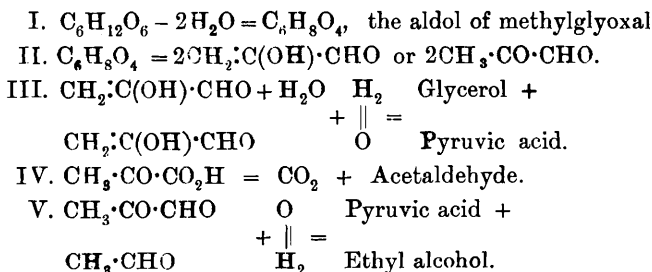
**Solubility of Sparingly Soluble Silver Salts Demonstrated by their Nucleus-destroying Action.** H. BECHHOLD (*Kolloid Zeitsch.*, 1919, **25**, 158—161).—*Staphylococcus* cultures in agar-jelly were partly covered with filter paper which had been coated with various sparingly soluble silver salts and left for four days in the dark at the ordinary temperature. The preparation was then placed in an incubator for forty-eight hours, and the area was

measured which was entirely free from the micro-organism. It is shown that the areas are practically proportional to the solubility of the salt employed. The experiments were carried out with metallic silver and the oxalate, oxide, carbonate, chromate, chloride, cyanide, thiocyanate, bromide, iodide, and sulphide. Similar experiments were carried out with metallic silver and silver chloride, but using cultures of various micro-organisms, and from the area of the free space deductions are drawn as to the resistance of these organisms to silver and silver chloride. In the case of metallic silver *B. pyocyaneus* is absolutely unacted on, and then follow in decreasing order of resistance, *B. coli*, the organism of swine erysipelas, *Staphylococcus*, paratyphoid, typhoid, and *B. proteus*. In the case of silver chloride the order is entirely different, the organism of swine erysipelas being most resistant, and this is followed in order by *B. pyocyaneus*, *Staphylococcus*, *B. proteus*, *B. coli*, paratyphoid, and typhoid. Except in the case of the organism of swine erysipelas, silver chloride is much more poisonous than metallic silver.

J. F. S.

**Further Experiments on the Correlative Formation of Acetaldehyde and Glycerol by the Scission of Sugar, and New Contributions to the Theory of Alcoholic Fermentation.**

CARL NEUBERG and ELSA REINFURTH (*Ber.*, 1919, 52, [B], 1677—1703. Compare A., 1914, i, 118).—As the result of the many investigations carried out by Neuberg and his co-workers in recent years, the following representation of the processes occurring in alcoholic fermentation is given:



According to this scheme, methylglyoxal and its corresponding acid, pyruvic acid, are intermediate compounds, and glycerol and acetaldehyde by-products in fermentation. The fact that methylglyoxal may be obtained from sugar by means of quite mild, alkaline agents (A., 1913, i, 1155) is suggestive, and led the authors to investigate the fermentation of sugar in the presence of such substances, especially as it had already been found that the activity of zymase is not impaired by such alkaline compounds (A., 1915, i, 1043). Preliminary experiments showed that the by-products, acetaldehyde and glycerol, become the chief products if sodium sulphite is the agent added (A., 1917, i, 502). This was explained by the formation of the very stable bisulphite compound (A., 1918,

i, 517), the corresponding compounds of dextrose or pyruvic acid being so easily dissociated that the reaction is not stopped until the acetaldehyde stage is reached. Owing to the arrest of the further reduction of the aldehyde, the available hydrogen must attack some other substance, leading, according to the above theory, to increased production of glycerol. This is now known to be actually the case, having by other workers been applied to the technical production of glycerol. In Neuberg's experiments it was found that for every molecule of acetaldehyde produced there is also one molecule of glycerol, the maximum yield of aldehyde being about 73%, and of glycerol about 70%, of that required by the equation  $C_6H_{12}O_6 = CH_3 \cdot CHO + C_3H_5(OH)_3 + CO_2$ .

An important confirmation of this theory of the action of the alkaline sulphite is the fact that neutral, insoluble sulphites, like those of calcium, magnesium, and zinc, and mixtures of sodium sulphite with phosphoric acid or sodium dihydrogen phosphate (that is, actually a feebly acid mixture) influence the course of the fermentation in the same way. In fact, the use of calcium sulphite is to be preferred in all such studies. Furthermore, the more dilute the solution is, the less marked is the effect of the sodium sulphite, even if the actual quantity present is 300% of the weight of the sugar.

The earlier experiments were performed with top yeast. The same results, at any rate in the presence of calcium sulphite, are given by bottom yeast, dried yeast, or maceration juice. In fact, the production of acetaldehyde (sodium nitroprusside-piperidine test) may be demonstrated in less than half an hour by incubating a mixture of 20 c.c. of 10% sucrose or dextrose, 2 grams of baker's yeast, and 2 grams of calcium sulphite (made from sodium sulphite and calcium chloride).

Some experiments on the fermentation of the trioses in the presence of calcium sulphite are also described. Dihydroxyacetone yields acetaldehyde, but disproportionate amounts of glycerol, sometimes higher than the expected quantities, whilst glyceraldehyde gives no acetaldehyde at all.

J. C. W.

**The Course of Alcoholic Fermentation in the Presence of Calcium Carbonate.** JOHANNES KERB (*Ber.*, 1919, 52, [B], 1795—1800).—Fernbach and Schön (*A.*, 1914, i, 237, 910) reported the production of a large amount of calcium pyruvate during the fermentation of dextrose or invert-sugar in the presence of calcium carbonate, which seemed incredible to the author, since he found that pyruvic acid and its salts are more rapidly fermented by yeast than sugar itself (*A.*, 1913, i, 1026). He has therefore tested the question, and finds that the production of alcohol by pure cultures of yeast is quite normal, and that no trace of a pyruvate is present in the soluble calcium salts formed. These consist of the sulphate, phosphate, hydrogen carbonate, and acetate. The only effect is that the yield of acetaldehyde and acetic acid is slightly greater. It is probable that Fernbach and Schön used an impure ferment which

produced a lactate and then pyruvate, that is, the normal alcoholic fermentation was very much suppressed.

J. C. W.

**The [Course of Alcoholic Fermentation in an Alkaline Medium. II. Fermentation with Living Yeast in Alkaline Solutions.** CARL NEUBERG and JULIUS HIRSCH (*Biochem. Zeitsch.*, 1919, **96**, 175—203. Compare A., 1917, i, 502).—In the fermentation of sugar by living yeast in the presence of sodium hydrogen carbonate a portion of the acetaldehyde which is formed as an intermediate product is not reduced to alcohol, but is converted into an equimolecular mixture of acetic acid and alcohol. An amount of glycerol equivalent to this portion of acetaldehyde is simultaneously produced.

S. S. Z.

**The Mechanism of the "Fixation" Method in the Degradation of Sugar into Acetaldehyde and Glycerol. The Correlation of Acetaldehyde and Glycerol during the Entire Process of Fermentation, the Time Factor in this Process and its Relation to Alcoholic Fermentation.** CARL NEUBERG and JULIUS HIRSCH (*Biochem. Zeitsch.*, 1919, **98**, 141—159).—At every stage during the process of fermentation of sugar in the presence of sodium sulphite, acetaldehyde and glycerol are produced in equimolecular proportions. As ethyl alcohol and carbon dioxide are also produced independently at the same time in equivalent proportions, the fermentation process can be followed by estimating the alcohol and aldehyde at the various stages.

S. S. Z.

**Utilisation of Amides by Yeast.** PIERRE THOMAS (*Ann. Inst. Pasteur*, 1919, **33**, 777—806).—Under suitable conditions, yeasts are capable of utilising carbamide, and to a lesser extent acetamide, as their source of nitrogen during the fermentation of sugar. Slight utilisation of propionamide and butyramide was indicated. The mechanism of this utilisation is not clear. Although all the experiments with carbamide indicate that the organic nitrogen is converted into ammoniacal nitrogen before utilisation, it was not possible to detect any urease or other such hydrolysing ferment either in the culture liquids or in the expressed cellular juice of the yeast.

W. G.

**Influence of Zinc Chloride on the Alcoholic Fermentation of Living and Killed Yeast.** S. KOSTYCHEV and L. FREY (*J. Russ. Bot. Soc.*, 1916, **1**, 39—47; from *Physiol. Abstr.*, 1919, **4**, 416).—Zinc chloride causes a production of acetaldehyde in "hefanol" and dry yeast, but not in living yeast. An important part of fermented sugar forms some compounds the structure of which is not yet known; acetaldehyde is formed only in presence of sugar; the quantity of carbon dioxide exceeds the quantity of alcohol.

J. C. D.

**The Action of Salts of Zinc and Cadmium on the Ferments of Yeast.** S. KOSTYCHEV and ZUBKOVA (*J. Russ. Bot. Soc.*, 1916, 1, 47—56; from *Physiol. Abstr.*, 1919, 4, 416).—The formation of acetaldehyde by dry yeast under the action of zinc salts depends on the influence of the zinc ion; a similar, but more energetic, effect can be produced by cadmium salts in the case of sugar fermentation, but not in the autolysis in water.

In the presence of cadmium salts, sucrose and lævulose produce a much larger quantity of acetaldehyde than dextrose. The reduction activity of yeast is very strongly inhibited by cadmium; the proteolytic ferments, on the contrary, show no change in their power either in the presence or absence of that metal. Salts of calcium, magnesium, strontium, mercury, aluminium, and antimony give no effects analogous to those produced by zinc and cadmium.

J. C. D.

**The Decomposition of Lactic Acid by Killed Yeast.** V. I. PALLADIN and D. A. SABYNIN (*Bull. Acad. Sci. Petrograd*, 1916, 187—194; from *Physiol. Abstr.*, 1919, 4, 417).—Lactic acid is decomposed by killed yeast in the presence of methylene-blue, and in a lesser degree in the presence of pyruvic acid; in the latter case, acetaldehyde is not produced. The authors believe that acetaldehyde plays a rôle of an acceptor of hydrogen, and is transformed into alcohol. Further work is necessary to determine whether lactic acid is an intermediate compound in the course of alcoholic fermentation.

J. C. D.

**The Influence of Alcohol and Methylene-blue on the Evolution of Carbon Dioxide by Killed Yeast.** V. I. PALLADIN and E. I. LOVCHINOVSKAIA (*Bull. Acad. Sci. Petrograd*, 1916, 253; from *Physiol. Abstr.*, 1919, 4, 416).—The experiments on the capacity of killed yeast to oxidise alcohol to carbon dioxide in the presence of an hydrogen acceptor failed.

J. C. D.

**The Yeast *Saccharomyces Thermantitonus*.** HANS VON EULER and INGVAR LAURIN (*Biochem. Zeitsch.*, 1919, 97, 156—170).—The inversion capacity, the catalase activity, the rate of fermentation at 35° and 40°, and the growth of *Saccharomyces thermantitonus* have been studied. The culture now examined showed certain deviations in its behaviour at the characteristic temperatures from the original culture (1905). It is suggested that adaptation may be responsible for this.

S. S. Z.

**Rôle Played by Water in the Processes of Alcoholic Fermentation and of Respiration of Plants.** V. I. PALLADIN (*Rec. d'art. dédié au Prof. C. Timiriazev*, 1916, 1—34; from *Physiol. Abstr.*, 1919, 4, 426).—The replacement of water, although only partial, by some other solvent, such as glycerol, ethylene glycol, formamide, pyridine, or ethyl alcohol, inhibits strongly the activity of zymase, carboxylase, and reductase. In the absence

of water there is no possibility for action of either ferments of alcoholic fermentation or of those of the anærobic phase of respiration. Water is assimilated during respiration, and is used for an anærobic oxidation of dextrose. The total carbon dioxide excreted at the time of respiration is of anærobic origin. Hydrogen, which is formed in higher plants during their respiration as a result of the anærobic decomposition of dextrose, is temporarily adsorbed by some special hydrogen acceptors (respiratory pigments). The total amount of oxygen adsorbed at the time of respiration is used exceptionally to oxidise hydrogen bound by hydrogen acceptors. Water produced during respiration is of anærobic origin. Anthocyanins play no immediate rôle in the respiratory process. Peroxydases serve for the formation of water and of pigments. The respiratory pigments play a rôle of mediators between the products of the anærobic decomposition of dextrose and peroxydases. The oxidation of chromogens follows the scheme of a moist auto-oxidation. Oxygen adsorbed at the time of respiration acts only as a hydrogen acceptor. Thus the majority of cases, if not all, in which the assimilation of atmospheric oxygen is accepted are in reality cases of an oxygen assimilation from water.

J. C. D.

**Apparatus for the Study of Photosynthesis and Respiration.** W. J. V. OSTERHOUT (*Bot. Gaz.*, 1919, 68, 60—62).—

A very simple apparatus is described and figured in the original, by means of which the air in a closed space, in which is present a branch or twig with green leaves and with the stem dipping into water, is caused to circulate through a solution of an indicator sensitive to carbon dioxide. By means of this the variation in the carbon dioxide concentration in the closed space may be followed, whilst the process of photosynthesis or the process of respiration is proceeding in the plant.

W. G.

**Carbon Dioxide and Plants. II.** E. REINAU (*Chem. Zeit.*, 1919, 43, 449—451, 489—491, 509—512, 524—525. Compare Klein and Reinau, A., 1914, i, 789).—From a lengthy review of the available data concerning the amount of carbon dioxide in the air, its fluctuations, and its effect on the growth of plants, the author is led to the following conclusions. Brown's theory of the internal pressure of carbon dioxide in plants containing chlorophyll is extended to the phenomena of assimilation under natural climatic conditions, and a mathematical expression is developed which takes into consideration the effect both of water and carbon dioxide on the growth of plants. The differences in concentration of these substances within and without the plant are regarded as differences of tension, the value of which appears to depend mainly on temperature and atmospheric humidity. Under climatic conditions, the amount of assimilation by green plants is not proportional to the absolute carbon dioxide content of the air, but to the difference in tension. The internal pressure of carbon dioxide

depends on the temperature, with rise of which it increases, and also on the illumination, with increase of which it falls. The two functions are explained by Willstätter's conception of the dual nature of chlorophyll; the presence of magnesium in the latter enables it to form a dissociating compound with carbon dioxide resembling a bicarbonate, whilst its chromophoric complex conditions its sensitiveness to light. The actual value of the carbon dioxide tension difference depends on the capacity of the air to receive water vapour, and therefore indirectly on the temperature, and this is explained by the close connexion which exists between the utilisation of the carbon, water, and salts within the plant.

The generally accepted idea that the plant is only able to utilise 0·5—1·0% of the light energy falling on it appears to be erroneous. Assimilation of carbon must proceed simultaneously with the evaporation of water; the latter process requires from 25·5% (in full sunlight) to 92·3% (in shade) of the energy derived from the sun by the leaf; the chlorophyll, in virtue of the power of selective light absorption exhibited by its chromophoric complex, converts about 7% of the light energy into chemical energy, and can utilise this amount completely in experimental cases and to the extent of 10—33% under climatic conditions.

The carbon dioxide content of the atmosphere is regulated by the activity of terrestrial green plants and of the sea on the one hand, and by that of humus (edaphon) on the other; this is rendered probable by the extreme sensitiveness of plants to alteration in the tension of carbon dioxide and by the fact that the action of green plants and "edaphon" is so nicely balanced that the actual quantity of carbon dioxide in the atmosphere is the expression of the dynamic equilibrium of the results of these two factors. Consequently, the absolute carbon dioxide content of the atmosphere is not a measure of the amount of carbon dioxide available for vegetation, but represents the proportion which cannot be lessened by plants under average conditions. It is conceivable that cases could arise in the open in which the plant suffers from too little carbon dioxide; the agricultural aspect of this possibility and the means of preventing it are discussed in the original paper, as is also the beneficent effect of an increased concentration of carbon dioxide on diseased plants.

Schlösing's theory of the regulation of the carbon dioxide content of the atmosphere by the ocean is regarded as not sufficiently firmly established, and as a partial aspect of the actual case.

H. W.

### **Formation of Inositol and Hexaldehyde in the Light.**

P. R. KÖGEL (*Biochem. Zeitsch.*, 1919, **97**, 21—23).—A theoretical paper. Inositol and hexaldehyde in the plant are formed by photosynthesis according to the following scheme:

Tetrahydroxyethylene →

hydrate of hexaketoexamethylene → inositol.

Inositol → cyclohexanone → hexaldehyde.



In a previous communication (A., 1919, i, 471) the author put forward a scheme in which he considered that tetrahydroxyethylene was an intermediate product in the formation of formaldehyde from carbon dioxide.  
S. S. Z.

**The Hydrocyanic Acid Question.** L. ROSENTHALER (*Schweiz. Apoth. Zeit.*, 1919, **57**, 267—270, 279—283, 295—297, 307—313, 324—329, 341—346; from *Chem. Zentr.*, 1919, iii, 274—275).—Dezani's supposed conversion of hydrocyanic acid into ammonia by the sap of plants is erroneous; its production is due to the hydrolysis of the cyanohydrins of sugar, and occurs under conditions which could not obtain in the plant. The author has been unable to detect any formation of ammonia from hydrocyanic acid in the cold, unchanged, and therefore acid, sap from the leaves of *Cornus sanguinea*, *Sambucus nigra*, etc. The presence of hydrocyanic acid, which is important from the point of view of Treub's hypothesis of nitrogen assimilation, has been detected with certainty in about 360 varieties in 148 species and 41 families; the varieties are enumerated in the original memoir, and particular reference is made to the distribution of the acid in the various parts of the plant. Generally, the presence of alkaloids and ethereal oils appears to be incompatible with the presence of hydrocyanic acid.

H. W.

### **Histological Investigations of Oxydases and Peroxydases.**

G. MARINESCO (*Compt. rend. soc. biol.*, 1919, **82**, 258—263; from *Chem. Zentr.*, 1919, iv, 173).—The presence of oxydases in the cells of various tissues can be detected histologically by the blue coloration of the cell granula when treated with solutions of  $\alpha$ -naphthol and *p*-phenylenedimethyldiamine. Since, however, fatty substances give a coloration with this reagent, a control with osmic acid and Nile-blue must be made in order to obtain an estimate of the actual amount of oxydase present. The presence of peroxydase can be detected by Perl's iron reaction, since its action is connected with the presence of this metal.

H. W.

### **The Constituents of Wood which give Colour Reactions. III.**

H. WICHELHAUS (*Ber.*, 1919, **52**, [B], 2054—2056. Compare A., 1916, i, 874; 1918, i, 151).—The active constituents have been removed from the distillates by extraction with ether and purified by distillation under greatly diminished pressure; two fractions, b. p. 88°/0.4 mm. and 95—105°/0.4 mm., are obtained, together with formic acid. Analyses of the fractions give results in agreement with those required by the formulæ  $C_{16}H_{22}O_9$  and  $C_{16}H_{22}O_{10}$  respectively, which are simply related to the formulæ of brazilin and hæmatoxylin.

H. W.

### **Some Components of Althæa (Marsh Mallow) Root.**

OSCAR VON FRIEDRICHS (*Arch. Pharm.*, 1919, **257**, 288—298).—Marsh mallow root contains 1.7% of an oil, consisting of glycerides of palmitic and oleic acids, together with butyric acid and a phyto-

sterol apparently identical with sitosterol; a hydroxy-acid of high molecular weight also appears to be present. The odour of the root is due to a substance of unknown composition, soluble in ether, insoluble in light petroleum, and non-volatile in a current of steam. The root contains a lecithin in which palmitic and oleic acids occur, and the base of which consists of choline. The sugar present is principally sucrose, of which the root contains 10.2%, the proportion of invert sugar being only 0.78%. The mucilage has the formula  $(C_6H_{10}O_5)_n$  and consists of glucosan (64%) and xylan. No galactose is present, but another saccharo-colloid, giving *d*-galactose on hydrolysis, is found.

T. H. P.

**The Saponins of *Chenopodium quinoa*, *Euphorbia helioscopia* (*Tithymatus helioscapius*), *Euphorbia Peplus*, and *Mercurialis perennis*.** M. GONNERMANN (*Biochem. Zeitsch.*, 1919, **97**, 24—40).—Preparations of the acid and neutral saponins of these plants have been investigated for their activity by hæmolysis of sheep's and human corpuscles. The titres are given.

S. S. Z.

**The Saponin in Fenugreek Seeds.** H. E. WUNSCHENDORFF (*J. Pharm. Chim.*, 1919, [vii], **20**, 183—185).—The saponin may be isolated by extraction with alcohol and precipitation by ether from the alcoholic solution; the substance consists of a semi-crystalline, white powder, m. p. 214—215°. On acid hydrolysis it yields a sapogenin and dextrose.

W. P. S.

**Endothia Pigments. II. Endothin-red.** L. E. SANDO (*Amer. J. Bot.*, 1919, **6**, 242—251; from *Physiol. Abstr.*, 1919, **4**, 350).—This pigment was obtained from the alcoholic extract of cultures of *Endothia fluens* grown on rice. Analysis and properties indicate a formula  $C_7H_5O$  and its probable relationship to the catechol group.

J. C. D.

**Chemistry of Heterotropic Phanerogams.** JULIUS ZELLNER (*Monatsh.*, 1919, **40**, 293—311).—A further extension and elaboration of the author's work on this subject (compare A., 1914, i, 913). Analysis of the ash of *Neottia nidus avis*, *Monotropa hypopitys*, *Cuscuta europaea*, *Lathraea squamaria*, and *Orobanche gracilis* discloses a high percentage of potassium, medium or small amounts of calcium, normal quantities of magnesium, and varying amounts of manganese which are probably connected with the presence of very active oxydases. The ratio of soluble nitrogen to total nitrogen is relatively high, but not the same for all parts of the plant. The question of the osmotic pressure of the cell sap is discussed, but, unfortunately, direct measurement is not yet possible. On various grounds, the author is led to the conclusion that heterotropic plants poor in chlorophyll are richer in osmotically active substances than are the green plants. Analyses show that in all probability the concentrations of cell sap in the parasite and host do not differ widely, in spite of the frequently great differences in water content.

The paper concludes with a critical review of the results obtained by the author and others in the study of the biochemistry of heterotrophic phanerogams. H. W.

**The Honey of the Poplar.** GEORGES TANRET (*Compt. rend.*, 1919, **169**, 873—874).—The sugary exudation on the leaves of *Populus nigra* contains three sugars, namely, melizitose, dextrose, and lævulose. W. G.

**The Colouring Matter of the Red Pea Gall.** MAXIMILIAN NIERENSTEIN (*T.*, 1919, **115**, 1328—1332).

**Function of Oxalic Acid in the Plant. The Enzymic Degradation of Oxalic Ions.** MARKUS STAEBELIN (*Biochem. Zeitsch.*, 1919, **96**, 1—50).—Various plants have been examined and found to contain an enzyme which acts on oxalic ions. It appears that the enzyme is fairly widespread in the plant kingdom, being also present in non-acid plants. It is found in most parts of the plant. The enzyme, which is an oxydase, also functions as a carb-oxy-lase converting a part of the oxalic ions into carbon dioxide. Its optimum temperature is 30—40°, and it is destroyed on boiling. It is active under ærobic conditions. In the leaves of *Rumex* the degradation of the oxalic ions proceeds according to the formula of a unimolecular reaction, whereas in the powdered leaves of *Helianthus* it functions in accordance with the law of autocatalysis. Its activity is retarded with increased concentration of oxalates.

S. S. Z.

**Chemical Composition of Natural and Polished Italian Rice. I.** GIOVANNI ISSOGLIO (*Atti R. Accad. Sci. Torino*, 1917—1918, **53**, 423—436).—The analytical results obtained by the author show that polished rice is very poor in ash and also in total phosphoric oxide, the phytin phosphoric oxide being reduced to a minimum. T. H. P.

**Chemical Composition of the Residues from the Treatment of Rice. II.** GIOVANNI ISSOGLIO (*Atti R. Accad. Sci. Torino*, 1918—1919, **54**, 440—451).—The rice offals derived from the husk are all very poor in nutritive substances. The residues obtained by removal of the outer cortical layers of the corns are, however, very rich in organic and inorganic phosphorus compounds, fats, and proteins, and contain phytin and vitamins. A third class of residues, composed of small, detached fragments of rice, together with foreign seeds, contains (1) products such as rice embryos, etc., which are used only as cattle feed, and (2) products which are similar in chemical composition to rice and are of value as human food. The results emphasise the necessity of reducing to a minimum the treatment to which rice is subjected. T. H. P.

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## Organic Chemistry.

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### Action of Selenyl Chloride on Unsaturated Compounds.

ARNO MÜLLER (*Chem. Zeit.*, 1919, **43**, 843).—Preliminary qualitative experiments show that selenyl chloride combines with unsaturated hydrocarbons and ketones to form well-defined, crystalline additive *compounds* which are somewhat unstable towards light and air, and are readily decomposed by boiling water into selenyl chloride and the corresponding hydrocarbon or ketone. Thionyl chloride also unites with olefinic substances to give small amounts of deeply coloured additive products, but the reaction is generally uncontrollably violent, and the formation of by-products cannot be avoided.

H. W.

### Removal of Aromatic Hydrocarbons from Mineral Oils by means of Trioxymethylene-sulphuric Acid.

JENŐ TAUSZ (*J. pr. Chem.*, 1919, [ii], **99**, 276—280).—Nastkujoff's formolite reaction (A., 1904, i, 801) for aromatic hydrocarbons is also shown by diolefines, such as methyl- and dimethyl-butadienes, which contain conjugated double bonds, owing to their condensation to ring compounds under the influence of sulphuric acid. On the other hand, the reaction is limited in the case of aromatic hydrocarbons to those containing a hydrogen atom in the nucleus, since hexamethyl- and hexaethyl-benzenes do not answer to it. Aromatic hydrocarbons are usually completely removed from mineral oils by this method, or by Herr's modification (A., 1910, ii, 904) only after a repetition of the treatment, owing to gradual dilution of the sulphuric acid. The author overcomes this difficulty by the use of trioxymethylene in place of formaldehyde solution or methylal. [See, further, *J. Soc. Chem. Ind.*, 1920, February.]

J. K.

### Action of Fluorine on Organic Compounds.

BURR HUMISTON (*J. Physical Chem.*, 1919, **23**, 572—577).—The action of fluorine on organic compounds is usually violent, leading to decomposition. Saturated hydrocarbons are ignited with incandescence and formation of free carbon, carbon fluorides, and hydrogen fluoride. "Filtchar" charcoal is attacked at the ordinary temperature, a gas, non-liquefiable at  $-80^{\circ}$ , being the chief product, accompanied by carbon tetrafluoride and tetrafluoroethylene (compare Moissan, A., 1890, 55). Selenium also yields as chief product a gas, which escapes liquefaction at  $-80^{\circ}$  (compare Prideaux, T., 1906, **84**, 316). Acetone is ignited by pure fluorine, whilst, in presence of an indifferent gas, charring takes place and some tetrafluoroethylene is produced. An indefinite product containing some carbonyl chloride is obtained from chloroform. Carbonyl chloride appears to be unattacked at  $6^{\circ}$ , but apparently some carbonyl fluoride is

produced at 200°. No evidence could be obtained of a reaction with carbon monoxide. Carbon tetrachloride is only slightly attacked at the ordinary temperature, but tetrachloroethylene gradually blackens even at 0°, hexachloroethane being among the products. J. K.

**Tetrachlorodinitroethane.** W. L. ARGO, E. M. JAMES, and J. L. DONNELLY (*J. Physical Chem.*, 1919, **23**, 578—585. Compare Biltz, A., 1902, i, 417).—Tetrachlorodinitroethane is very soluble in liquid nitrogen tetroxide, and has pronounced toxic and lachrymatory properties. The optimum temperature for its production from dry liquid nitrogen tetroxide and tetrachloroethylene is 80°. [See, further, *J. Soc. Chem. Ind.*, 1920, 82A.] J. K.

**Preparation of Ethyl Alcohol.** ELEKTRIZITÄTSWERK LONZA (Brit. Pat. 134521).—In the catalytic reduction of acetaldehyde to ethyl alcohol by means of hydrogen, the excess being returned to the operation by a circulating device (Brit. Pat. 120163), the production of ethyl ether as a by-product, and the gradual poisoning of the catalyst by the decomposition products of acetaldehyde, are avoided by circulating with the hydrogen an amount of oxygen not exceeding 0.3%. The temperature of the reaction chamber is maintained between 90° and 170° by cooling, or preferably by using the hydrogen in such excess that it absorbs and removes the superfluous heat of the reaction. Whereas without the use of oxygen the yield of alcohol fell after thirty hours nearly to zero, an average yield of 95% of the alcohol theoretically possible was obtained in a run extending over two hundred and eleven hours, in which 0.15% of oxygen was used. This beneficial effect of the oxygen cannot be attributed to the complete oxidation of carbon monoxide, methane, etc., to the presence of which the injurious effect on the catalyst is ascribed. G. F. M.

**Melissyl Alcohol and Melissic Acid.** A. HEIDUSCHKA and M. GAREIS (*J. pr. Chem.*, 1919, [ii], **99**, 293—311).—The formula for melissyl alcohol has been considered by some workers to be  $C_{30}H_{61}\cdot OH$ , by others  $C_{31}H_{63}\cdot OH$ . The authors have therefore prepared a series of derivatives of melissyl alcohol from carnauba wax and from beeswax, and confirmed the view of Schwalb (A., 1885, 962) that the alcohols from these sources differ. The former has the formula  $C_{30}H_{61}\cdot OH$ , whilst that of the latter is  $C_{31}H_{63}\cdot OH$ . The melting points of their respective derivatives were as follows (those of carnauba melissyl alcohol being quoted first): *acetates*, 74° and 70°; *benzoates*, 69.5° and 66°; *phthalates*, 82° and 81.5°; *monochloroacetates*, 79.5° and 74°; *phenylurethanes*, 98° and 96°; *chlorides*, 67° and 65°; *bromides*, 68° and 67°; *iodides*, 69.5° and 68°. Carnauba melissyl alcohol on oxidation by Hell's process (A., 1884, 1433) gave a melissic acid,  $C_{30}H_{60}O_2$ , m. p. 90° (lead salt, m. p. 118°), whilst the acid,  $C_{31}H_{62}O_2$ , from beeswax had m. p. 88.5° (lead salt, m. p. 115°). The latter acid was also obtained by

hydrolysis of carnauba melissyl cyanide, which in an impure condition melted at  $75^{\circ}$ .

Stürcke's observation (A., 1884, 1280) that carnauba melissyl alcohol is accompanied by an alcohol,  $C_{27}H_{56}O$ , m. p.  $76^{\circ}$ , was also confirmed. J. K.

### Phytochemical Reduction of Ketones. Biochemical Preparation of Optically Active Secondary Alcohols.

C. NEUBERG and F. F. NORD (*Ber.*, 1919, **52**, [B], 2237—2248). The authors find that the phytochemical reduction of the ketonic group is frequently possible both with aromatic and aliphatic ketones, and leads to the production of the corresponding secondary alcohols. Hydrogenation is more difficult than with the aldehydes, since it proceeds more slowly and less completely, and also requires more energetic conditions. The biological nature of the process is shown by the fact that the secondary alcohols are optically active, an asymmetric carbon atom being developed during the process. They have been isolated in the chemically pure condition, but the yields are poor (about 10%) and a considerable portion of the original material remains unattacked, and is subsequently removed by treatment with sodium hydrogen sulphite or hydrazine bases. They are not optically pure. Acetaldehyde is invariably also formed, the oxidative production of which is probably the complementary process of the hydrogenation of the ketone.

The mixtures were generally made from conductivity water (2 litres) at  $35$ — $40^{\circ}$ , sucrose (200 grams), yeast (200 grams) and the ketone (10—15 grams), and fermentation was allowed to proceed for three to six days, frequently followed by a second addition of sucrose and yeast and renewed fermentation. In this manner methyl ethyl ketone yielded *d*-methylethylcarbinol, b. p.  $99$ — $100^{\circ}$ ,  $[\alpha]_D + 3.34^{\circ}$ , methyl *n*-propyl ketone gave *d*-methyl *n*-propylcarbinol, b. p.  $117$ — $119^{\circ}$ ,  $[\alpha]_D^{16} + 6.3^{\circ}$ ,  $D^{16} 0.810$ , methyl *n*-hexyl ketone yielded *d*-methylhexylcarbinol, b. p.  $177$ — $179^{\circ}$ ,  $[\alpha]_D^{16} + 2.85^{\circ}$ , whilst *d*-methylnonylcarbinol, b. p.  $228$ — $229^{\circ}$ ,  $[\alpha]_D^{16} + 2.95^{\circ}$ , and *l*-phenylmethylcarbinol, b. p.  $202$ — $204^{\circ}$ ,  $[\alpha]_D^{16} - 8.01^{\circ}$ , were prepared from methyl nonyl ketone and acetophenone respectively. H. W.

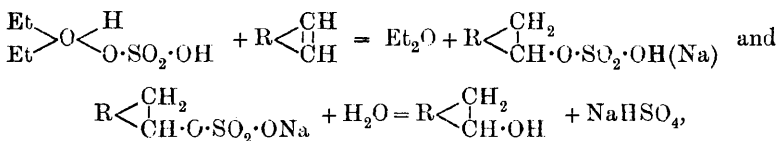
**Phytochemical Reduction of Diketones.** C. NEUBERG and F. F. NORD (*Ber.*, 1919, **52**, [B], 2248—2254. Compare preceding abstract).—The authors find that diacetyl can be readily hydrogenated by biochemical methods, and that *l*- $\beta$ -butylene glycol is produced in yield which is regarded as satisfactory when the difficulties of isolation are taken into consideration; the optical activity of the product is the more remarkable, since Harden and Walpole have found that the action of bacteria on a series of carbohydrates leads to a mixture of the racemic and meso-forms of the glycol. Under similar circumstances, benzil yields benzoin, which in the main is optically inactive, but which contains small amounts of *l*-benzoin. Attempts to reduce benzil or benzoin to the corresponding glycol were unsuccessful. H. W.

### Addition Catalysis by means of Diethyloxonium Salts,

$\text{Et} > \text{O} < \begin{smallmatrix} \text{H} \\ \text{R} \end{smallmatrix}$ . OSSIAN ASCHAN (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 8, 1—32).—Reference is first made to the use of ethereal solutions of hydrogen chloride in the synthesis of hydrochlorides in the terpene series (compare A., 1916, i, 51), and it is pointed out that without the use of ethyl ether as catalyst tertiary pinene hydrochloride (*Öfvers. Finska Vet-Soc. förh.*, 1914—1915, **57**, [A], No. 1) could not have been prepared. The results thus obtained with the ether-additive product of hydrogen chloride led the author to investigate the addition of water to unsaturated compounds by means of a mixture of absolute ether and sulphuric acid monohydrate. When this mixture is made there is a large development of heat, and when the two components are in equivalent quantities the resulting mixture is much more viscous than the sulphuric acid. It is concluded that diethyloxonium sulphate,  $\text{OHEt}_2 \cdot \text{O} \cdot \text{SO}_2 \cdot \text{OH}$ , is formed, although neither it nor a salt could be isolated.

The method of experiment was generally to dissolve the sulphuric acid monohydrate in the molecular quantity of ethyl ether, or, if necessary, in an excess of ether, well cooling meanwhile, and then add the unsaturated compound in small portions at a time, again well cooling. In some experiments a further quantity of water was added to the sulphuric acid monohydrate. After keeping for some time the resulting mixture was poured into an excess of sodium carbonate solution and the products isolated by steam distillation and subsequent fractionation.

The normal reaction would be represented by the equations:



the alcohol being produced, but in some cases, possibly when the reaction mixture is poured into the sodium carbonate solution, fission of water takes place with reproduction of the original compound or an isomeride; di- and poly-terpenes may also be produced.

Camphene hydrate and santenol, which are among the lesser sensitive alcohols, are the main products of reaction from camphene and santene, but some of the original substances are re-formed, either as such or as diterpenes. The more sensitive alcohols, which should result from such substances as pinene, nopinene, etc., are not produced, either the original compound being re-formed or else a polymerisation product obtained. In the case of  $\beta$ -methyl- $\Delta^{\beta}$ -butylene, the dipolymeride, diamylene, is readily obtained in an almost pure condition, together with smaller quantities of tertiary isoamyl alcohol.

Absolute ethyl ether and colourless concentrated nitric acid, when mixed in small quantities, give a mixture, which is stable for a

short time. Diethyloxonium nitrate may be present in such a mixture. T. S. P.

### Kephalin. VII. The Glycerophosphoric Acid of Kephalin.

P. A. LEVENE and IDA P. ROLF (*J. Biol. Chem.*, 1919, **40**, 1—16).—The generally accepted formula of kephalin presumes the existence of glycerophosphoric acid in the molecule, but the experimental evidence produced so far in support of this supposition is not convincing. The presence of glycerol in kephalin has been satisfactorily demonstrated (Foster, A., 1915, ii, 493). Theoretically, there are only two alternative ways in which glycerol may be attached to phosphoric acid, either directly with the formation of glycerophosphoric acid, or indirectly with the glycerol attached to the aminoethyl alcohol. If the latter condition existed, the amino-group of the kephalin molecule would not be free. Since it has been experimentally shown that the amino-group is free, it follows that the presence of glycerophosphoric acid in kephalin could have been accepted before the substance was actually isolated.

The glycerophosphoric acid isolated from the hydrolysis of kephalin possesses an optical rotation of the same magnitude as the acid from lecithin, namely,  $[\alpha]_D^{20} = -0.69^\circ$ . This work establishes the fact that glycerophosphoric acid exists in kephalin, and that the acid is identical with that present in lecithin. The crude barium glycerophosphate from kephalin shows dextrorotation, which may account for the statement made by Fränkel and Dimitz (A., 1909, i, 870) that the glycerophosphoric acids present in lecithin and kephalin are optical isomerides. The authors have now shown, however, that on purification the dextrorotation is lost. It is probably due to admixture of the barium glycerophosphate with a dextrorotatory product of intermediary hydrolysis. The authors are unable to confirm the observations of Willstätter and Lüdecke, who stated that the optical rotation of the glycerophosphoric acid from lecithin differs according to the mode of preparation. The maximum rotation for the glycerophosphoric acid from lecithin is found to be  $[\alpha]_D^{20} - 0.74^\circ$ , a value lower than that recorded by Willstätter and Lüdecke (A., 1904, i, 1067).

J. C. D.

### The History of Zeise's Mercaptan and its Name (1833).

PAUL DIERGART (*J. pr. Chem.*, 1919, [ii], **99**, 281—292).—Historical. J. K.

### Preparation of Ethylene Ethylidene Disulphide. OSKAR

MATTER (D.R.-P. 313650; from *Chem. Zentr.*, 1919, iv, 617—618).—When the amorphous ethylene sulphides,  $(C_2H_4S)_x$ , m. p.  $145^\circ$  and  $176^\circ$  respectively (prepared by the action of ethylene chloride or bromide on aqueous or alcoholic solutions of alkali sulphides), are heated almost to dull redness in the absence of air, the main portion distils as *ethylene ethylidene sulphide*, leaving only an unimportant charcoal-like residue. Decomposition occurs more smoothly when a solid substance, such as a metallic sulphide, is



added to the ethylene sulphide and when a slow current of hydrogen sulphide is sent through the apparatus. After being frozen out, the crude material is purified by passage through a tube loosely packed with fragments of porous pot and heated at about  $300^{\circ}$ . The vapours are collected in a well-cooled receiver. Ethylene ethylidene disulphide, after being shaken with aqueous alkali, is obtained as an almost colourless liquid, b. p.  $172-173^{\circ}$ , which is a good solvent for organic substances and may serve as a basis for pharmaceutical preparations. H. W.

**Volatility with Steam of Lower Fatty Acids in Dilute Aqueous Solution.** EDGAR J. WITZEMANN (*J. Amer. Chem. Soc.*, 1919, **41**, 1946—1951).—The volatility in steam of formic acid, acetic acid, propionic acid, and butyric acid has been examined by distilling equivalent solutions (about 1%) and analysing the distillates. The volatility is shown to increase with increasing molecular weight. Thus the first fraction (20 c.c.) to distil over contains 6.92% of the acetic acid, 3.94% of the formic acid, 12.4% of the propionic acid, and 19.5% of the butyric acid, whilst the residue (15 c.c.), after distillation of 180 c.c., contains 36.8% of the formic acid, 18.6% of the acetic acid, 5.7% of the propionic acid, and 1.4% of the butyric acid. This behaviour is explained as due to the hydration of the acids to form stable complexes, which lower the vapour pressure of the solution. The addition of potassium chloride or magnesium chloride to solutions of formic or acetic acid increases the volatility of the acids. The increase in volatility depends on the concentration of the salt, and also on its nature. Thus 0.5*N*-potassium chloride has about the same effect as 0.2*N*-magnesium chloride. Using a series of salts in 0.25*M* quantities in formic acid solution, the volatility in steam is increased in every case, the order being an increasing volatility with decreasing electro-affinity of the metallic ion of the salt for the chlorides of potassium, sodium, barium, strontium, calcium, magnesium, and aluminium. The chlorides of iron, manganese, and copper are irregular in their action. J. F. S.

**The Chlorination of Methyl Formate and Chloroformate.** V. GRIGNARD, G. RIVAT, and ED. URBAIN (*Compt. rend.*, 1919, **169**, 1074—1077. Compare Kling, Florentin, Lassieur, and Schmutz, this vol., i, 8).—Light exerts a marked influence on the chlorination of methyl chloroformate. In diffused light it is only the chloromethyl ester which is formed, bright sunlight being necessary for the formation of the di- or tri-chloromethyl ester. In ultra-violet light the trichloro-ester is easily obtained. The effect of temperature is such that up to  $110-112^{\circ}$  the chlorination proceeds smoothly, but at  $113-114^{\circ}$  it slackens very noticeably and at  $117^{\circ}$  decomposition begins to take place with the formation of carbonyl chloride.

Catalysts, such as ferric chloride, antimony chloride, etc., are beneficial at first in the formation of the dichloromethyl ester, but

when a certain concentration is reached decomposition commences, and may continue indefinitely, as some of the perchloride becomes dissolved in the liquid and continues its action. W. G.

**The Chloro-derivatives of Methyl Formate and Methyl Carbonate.** V. GRIGNARD, G. RIVAT, and ED. URBAIN (*Compt. rend.*, 1919, **169**, 1143—1147. Compare this vol., i, 8, and preceding abstract).—A study of the properties of the chloromethyl chloroformates and of chloro-derivatives of methyl carbonate.

Chloromethyl chloroformate,  $\text{ClCO}_2\cdot\text{CH}_2\text{Cl}$ , is a lachrymatory liquid and has b. p.  $106.5^\circ$ ,  $D^{14}_D 1.456$ ,  $n^{20}_D 1.42857$ . Dichloromethyl chloroformate is a lachrymatory liquid, b. p.  $46^\circ/62$  mm. and  $111^\circ$ ,  $D^{17}_D 1.558$ ,  $n^{22}_D 1.44322$ . Trichloromethyl chloroformate is less lachrymatory but more suffocating than the two preceding esters, and has b. p.  $125\text{—}126^\circ/748$  mm.,  $D^{15}_D 1.644$ ,  $n^{20}_D 1.45664$ .

By moderate chlorination of methyl chloroformate in diffused sunlight *trichloromethyl carbonate*, b. p.  $138^\circ$ ,  $D^{22.5}_D 1.297$ ,  $n^{20}_D 1.41160$ , is obtained as one of the products. *Dichloromethyl methyl carbonate* has b. p.  $48\text{—}49^\circ/18$  mm.,  $D^{17}_D 1.412$ ,  $n^{20}_D 1.42852$ . *Chloromethyl dichloromethyl carbonate*, one of the products of the more intense chlorination of methyl chloroformate, has b. p.  $96^\circ/45$  mm. and  $177\text{—}179^\circ$ ,  $D^{18}_D 1.553$ ,  $n^{20}_D 1.45414$ . Methyl trichloromethyl carbonate has b. p.  $59.5\text{—}60^\circ/16$  mm. and  $161\text{—}163^\circ$ ,  $D^{17}_D 1.525$ ,  $n^{20}_D 1.44964$ . *s-Tetrachloromethyl carbonate*, b. p.  $83^\circ/19$  mm. or  $93\text{—}94^\circ/20$  mm.,  $D^{18}_D 1.630$ ,  $n^{20}_D 1.46306$ , is one of the products of the chlorination of methyl chloroformate in a leaden vessel. By carrying the chlorination still further, hexachloromethyl carbonate, m. p.  $79^\circ$ , is obtained. W. G.

**Properties of the Chloromethyl Chloroformates.** ANDRÉ KLING, D. FLORENTIN, A. LASSIEUR, and E. SCHMUTZ (*Compt. rend.*, 1919, **169**, 1166—1168).—A study of the physical and chemical properties of the mono-, di-, and tri-chloromethyl chloroformates.

The purest specimen of chloromethyl chloroformate contained 8.6% of the dichloromethyl ester. It had b. p.  $52.5\text{—}53^\circ/100$  mm. and  $106.5\text{—}107^\circ/700$  mm.,  $D^{15}_D 1.465$ . It is both lachrymatory and suffocating. It is quantitatively decomposed by water according to the equation  $\text{Cl}\cdot\text{CO}_2\cdot\text{CH}_2\text{Cl} + \text{H}_2\text{O} = \text{H}\cdot\text{CHO} + \text{CO}_2 + 2\text{HCl}$ . With alcohols it gives the corresponding mixed chloromethyl carbonates, and with sodium phenoxide it gives *phenyl chloromethyl carbonate*, b. p.  $122\text{—}124^\circ/13$  mm.,  $D^{23}_D 1.255$ . Anhydrous aluminium or ferric chloride decomposes chloromethyl chloroformate at  $70^\circ$ , giving carbonyl chloride.

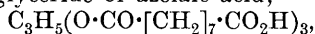
Dichloromethyl chloroformate has b. p.  $54\text{—}55^\circ/100$  mm. and  $110\text{—}111^\circ/700$  mm.,  $D^{15}_D 1.560$ . On hydrolysis it yields carbon monoxide, carbon dioxide, and hydrogen chloride. With alcohols it gives the mixed dichloromethyl carbonates, and with sodium phenoxide *phenyl dichloromethyl carbonate*, m. p.  $14.5^\circ$ , b. p.  $124\text{—}125^\circ/14$  mm.,  $D^{15}_D 1.34$ .

Trichloromethyl chloroformate has b. p.  $49^{\circ}/50$  mm. and  $127^{\circ}/750$  mm.,  $D^{15}_4$  1.653. Its general properties resemble those of carbonyl chloride. On hydrolysis it gives carbon dioxide and hydrogen chloride, and with aniline water it yields *s*-diphenylcarbamide. With alcohols it gives the mixed trichloromethyl carbonates, and with sodium phenoxide yields *phenyl trichloromethyl carbonate*, m. p.  $166^{\circ}$ .

Anhydrous aluminium or ferric chloride decomposes it, giving carbon tetrachloride and carbon dioxide. W. G.

### Determination of the Position of the Double Linking and its Transposition in some Unsaturated Compounds.

(MLLE.) A. C. NOORDUYN (*Rev. trav. chim.*, 1919, **38**, 317—344).—The method adopted was to convert the unsaturated compound into its ozonide and decompose this by boiling it with water, the resulting aldehydes being, if necessary, oxidised to the acids for purposes of identification. By this method Goldsobel's formula for ricinoleic acid,  $\text{CH}_3\cdot[\text{CH}_2]_5\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot[\text{CH}_2]_7\cdot\text{CO}_2\text{H}$  (compare A., 1895, 81), has been confirmed. Further evidence in support of this was obtained by the ozonisation of castor oil and subsequent decomposition of the ozonide. One of the products of this action, after oxidation, was the glyceride of azelaic acid,



$D^{15}_4$  1.0377,  $n$  1.4693. Similarly, undecenoic acid was shown to have the formula  $\text{CH}_3\cdot\text{CH}\cdot[\text{CH}_2]_8\cdot\text{CO}_2\text{H}$ , and one of the products of decomposition of its ozonide was the semi-aldehyde of sebacic acid, m. p.  $126^{\circ}$ , giving a *semicarbazone*, m. p.  $168^{\circ}$ .

Three unsaturated hydrocarbons, octylene, decylene, and heptadecylene, were prepared by the method of Grosjean (compare A., 1892, 691) by heating the barium salt of the next higher acid with sodium ethoxide, and it was shown by the ozonide method that the products, in every case, were mixtures of isomeric hydrocarbons. Similarly, the  $\beta$ -octylene of Kahlbaum, prepared by the action of zinc chloride on secondary octyl alcohol, was shown to be a mixture of isomerides.

By the fusion of oleic acid with potassium hydroxide there is formed not only acetic and palmitic acids, but a number of higher homologues of acetic acid and lower homologues of palmitic acid. Under similar conditions elaidic acid also gives a mixture of acids.

W. G.

**Ghedda or East Indian Wax. II. Its Acids.** A. LIPP and EUGEN KOVÁCS (*J. pr. Chem.*, 1919, [ii], **99**, 243—255. Compare A., 1912, i, 675).—The residue of potassium salts, after removal from the wax of alcohols and hydrocarbons in the manner previously described, furnished a mixture of acids, of which one was sparingly soluble in ether (see following abstract). From the remainder, after removal by steam of small amounts of formic and butyric acids, margaric acid and a previously unknown hydroxy-

margaric acid were separated by fractional extraction with light petroleum.

*Hydroxymargaric acid*,  $C_{17}H_{34}O_3$ , m. p.  $58^\circ$ , could not be distilled under reduced pressure. It was characterised as a normal acid by conversion into margaric acid through the action of hydriodic acid successively at  $100^\circ$  and at  $200$ – $220^\circ$ . The intermediate iodomargaric acid was only obtained impure in the form of needles, m. p.  $41.5^\circ$ . J. K.

**Ghedda or East Indian Wax. III. Hydrocarbons and Acids.** A. LIPP and E. CASIMIR (*J. pr. Chem.*, 1919, [ii], 99, 256–258).—The wax contains approximately 48% of ceryl alcohol, 7% of hydrocarbons (5% of heptacosane, 2% of hentriacontane, with traces of a hydrocarbon of low melting point), 24–25% of hydroxymargaric acid, m. p.  $55$ – $56^\circ$  (see preceding abstract), 1.5–2% of an isomeric hydroxymargaric acid, m. p.  $71$ – $72^\circ$ , 9–10% of margaric acid, 8–9% of palmitic acid, 2% of “Ghedda” acid, and 1% of cerotic acid with traces of formic, acetic, and butyric acids and tarry matter. Cerotic and ghedda acids are present mainly in the free condition, the others in the form of their ceryl esters.

“Ghedda” acid, to which the formula  $C_{34}H_{68}O_2$  is provisionally ascribed, m. p.  $94.5$ – $95^\circ$ , forms mossy aggregates of white needles. Its sparing solubility in ether and that of its potassium salt in alcohol permit its separation from the other acids present. It differs from melissic acid, but is possibly identical with an acid obtained by Schalfeieff (this Journ., 1877, i, 454; compare, however, Nafzger, A., 1884, 1297).

*Hydroxymargaric acid*,  $C_{17}H_{34}O_3$ , m. p.  $71$ – $72^\circ$ , forms needles or leaflets, and was isolated from the last light petroleum extracts of the mixed acids (see preceding abstract). Its calcium salt,  $Ca(C_{17}H_{33}O_3)_2$ , forms small, spherical nodules.

The hydrocarbon previously described (Lipp and Kuhn, A., 1912, i, 675) as  $C_{30}H_{62}$ , m. p.  $70^\circ$ , is now found to have m. p.  $68$ – $68.5^\circ$ , and considered to be hentriacontane,  $C_{31}H_{64}$ , from its resemblance to the hydrocarbon obtained by Krafft from palmitone (A., 1882, 1272) and its identity with that prepared by Popp (*Diss., Tech. Hochschule*, Munich, 1916), by reducing myricyl alcohol, which, on the other hand, he oxidised to melissic acid, at the same time establishing the formula  $C_{31}H_{62}O_2$  for this acid (but see Heiduschka and Gareis, this vol., i, 134). Also the hydrocarbon,  $C_{26}H_{54}$ , m. p.  $58^\circ$ , is now found to have m. p.  $59.5^\circ$ , and considered to be heptacosane,  $C_{27}H_{56}$ , from its similarity to the hydrocarbon obtained from myristone by Krafft (*loc. cit.*). J. K.

**Crystallographic Investigation of the Dichlorosuccinic Acids.** G. AMINOFF (*Arkiv Kem. Min. Geol.*, 1917–18, 7, No. 9, 1–11).—The optically active dichlorosuccinic acids have m. p.  $166$ – $167^\circ$  and  $D^{15}_D 1.820$ . They are monoclinic-sphenoidal [ $a:b:c=2.3351:1.2:3.754$ , and  $\beta=101^\circ 30'$ ]. Twinning takes place along the plane  $c\{001\}$ , cleavage parallel with  $x\{\bar{1}01\}$ , and optical

extinction parallel to the edges  $[(100):(001)]$  and  $[(001):(011)]$ . The plane of the optical axis is parallel with  $b\{010\}$ .

The racemic acid has m. p. 174—175° and  $D^{15}_D$  1.844. The crystals are monoclinic-prismatic,  $[a:b:c=0.5846:1:0.5994]$  and  $\beta=100^\circ 46'$ . Cleavage takes place parallel to the axes  $x\{101\}$  and  $b\{010\}$ , and optical extinction parallel with the edges  $[(100):(001)]$  and  $[(001):(010)]$ . The optical axis is parallel with  $b\{010\}$ . It is not certain from the results whether the racemic acid is a true racemate.

*meso*-Dichlorosuccinic acid has m. p. 217—218°. The crystals are monoclinic and needle-shaped, but they were not well enough developed to determine the crystallographic constants. T. S. P.

**Apparatus for the Electrolytic Decomposition of Organic Acids at Low Temperature and with Small Volumes of Liquid. Electrolytic Decomposition of the Alkali Salts of Citraconic Acid.** F. HENRICH and WILHELM SCHENK (*Ber.*, 1919, 52, [B], 2120—2125).—The apparatus consists of a small flask, the bottom of which has been removed and the neck of which is provided with a cork holding a small inverted tube. The latter serves the two-fold function of diminishing the size of the apparatus to the required extent and of allowing efficient cooling by the introduction of a stream of cold water into the tube. As anode, a stout platinum wire or, preferably, a platinum gauze, is placed in close proximity to the tube. The cathode consists of a piece of nickel gauze. The apparatus is conveniently kept at a temperature of 25—40°. A gas-holder of the type previously recommended by Henrich (*A.*, 1909, ii, 66) is used for collection of the anode gases, and arrangements are also described which permit the analysis of these gases at any desired moment.

Electrolysis of concentrated, faintly alkaline solutions of potassium citraconate yields a mixture of oxygen, carbon dioxide, and allylene at the anode, the proportion of the latter increasing with increasing strength of current. Its production is also favoured by high concentration and low temperature, and is found to depend on the particular alkali salt used; the yields increase from lithium through sodium and potassium to rubidium, and then decline to caesium. The authors consider that this behaviour supports the conception of Fichter and Krummenacher (*A.*, 1918, i, 369) that electrolytic decomposition of organic acids is an oxidation process rather than the purely ionic hypothesis of Crum-Brown and Walker.

H. W.

**Electrolytic Decomposition of Glutaconic Acid.** F. HENRICH and ADOLF HERZOG (*Ber.*, 1919, 52, [B], 2126—2130).—The electrolytic decomposition of alkaline solutions of potassium glutaconate in the apparatus described in the preceding abstract leads to the formation of acetylene, acraldehyde, carbon monoxide, and carbon dioxide at the anode, these appearing to be the sole products of the action; the mechanism of the change has not been

fully elucidated, but the results appear to support the oxidation theory of electrolytic decomposition advanced by Fichter and Krummenacher (A., 1918, i, 369).  
H. W.

**Glutaconic Acid. III. Condensation of Sodioformylacetic Ester with Cyanoacetic Ester.** P. E. VERKADE (*Vers. Akad. Wetensch. Amsterdam*, 1919, 27, 1130—1139).—The product of reaction of these two substances is not ethyl  $\alpha$ -cyano-glutaconate, as stated by other workers, but probably ethyl  $\omega\omega'$ -dicyano-1:3-dimethylcyclobutane- $\omega:\omega':2:4$ -tetracarboxylate.

CHEMICAL ABSTRACTS.

**Preparation of Gluconic Acid.** A. HERZFELD and G. LENART (*Zeitsch. Ver. deut. Zuckerind.*, 1919, 122—128).—Kiliani and Kleemann's method (A., 1884, 993) has been modified in the following manner, so that the use of lead compounds for the elimination of the hydrobromic acid is obviated, the object in view being the elaboration of a technical process for the preparation of a substitute for vegetable acids. One part of dextrose (from starch), dissolved in 5 parts of water, is shaken in a closed vessel with 1 part of bromine until the disappearance of the latter. Oxidation is generally complete after twenty-four hours, at the end of which time the excess of bromine is distilled off in a vacuum, the temperature of the water-bath being about 50°. Heating is continued until the liquid commences to be coloured, when it is diluted with about 350 times its volume of water, and the hydrobromic acid neutralised by sodium carbonate. An excess of calcium carbonate is added gradually at a temperature of 90° (during which operation any lactone formed during distillation is transformed), and after two or three days the calcium salt separates out, and is recrystallised. By working up the mother liquors an almost quantitative yield may be obtained. If invert sugar is used in place of dextrose, the unchanged lævulose may be either precipitated as its insoluble calcium salt or converted into lævulic acid by boiling with dilute mineral acid.  
J. P. O.

**The Hydrates of Heptaldehyde.** (Mlle.) A. C. NOORDUYN (*Rec. trav. chim.*, 1919, 38, 345—350).—An examination of the system heptaldehyde-water shows the existence of a monohydrate and a dihydrate. No evidence of the existence of the hemihydrate described by Bussy (*Annalen*, 1846, 60, 247) could be obtained.

W. G.

**The Stabilisation of Acraldehyde. IV. Compounds Acting as Stabilisers against the Formation of Disacryl.** CHARLES MOUREU, CHARLES DUFRAISSE, and PAUL ROBIN (*Compt. rend.*, 1919, 169, 1068—1072. Compare A., 1919, i, 574; this vol., i, 10).—A study of the products present in the various fractions obtained by the fractional distillation of acraldehyde prepared by the dehydration of glycerol with potassium hydrogen sulphate shows that benzoic acid exerts a marked but variable stabilising action.

Phenol, found in some of the fractions, is also a stabilising agent, but its activity is relatively feeble. W. G.

**The Stabilisation of Acraldehyde. V. Stabilising Action of Substances with a Phenolic Group.** CHARLES MOUREU, CHARLES DUFRAISSE, PAUL ROBIN, and JEAN PUGNET (*Compt. rend.*, 1920, **170**, 26—31. Compare preceding abstract).—It has previously been shown that both phenol and benzoic acid exert a marked stabilising action against the formation of disacryl from acraldehyde. The study has now been extended to other phenols and certain hydroxy-acids.

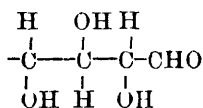
Of the monohydroxyphenols examined,  $\alpha$ -naphthol shows the strongest stabilising action, and the presence of several hydroxy-groups attached to ring carbon atoms causes a notable increase in the stabilising power, except when two hydroxy-groups are in the meta-position to one another. The action of the various hydroxy-benzoic acids is intermediate between that of the phenol and that of benzoic acid itself. Unlike the phenols, their methyl ethers or their acetyl derivatives show little or no stabilising action. Similarly, the alcohols and the polyhydric alcohols do not exercise any stabilising action. Not only do the polyphenols inhibit the formation of insoluble resin (disacryl) from acraldehyde, but they also exercise a similar inhibiting action against the formation of soluble resin, even when the phenol is only present to the extent of 1 in 4000. W. G.

**Oxidation of Mannitol by Nitrous Fumes.** E. VOTOČEK and C. KRAUZ (*Zeitsch. Zuckerind. Böhm.*, 1919, **43**, 577—580).—In the hope of finding a reagent which will effect the oxidation of polyhydric alcohols to either aldehydic or ketonic substances exclusively, the authors have investigated the action of nitrous fumes on an aqueous solution of mannitol; oxidation occurs slowly (but can be accelerated by the addition of a small quantity of a ferrous salt) and leads to the formation of a mixture of mannose and lævulose. H. W.

**Oximes of Rhodeose and Fucose.** E. VOTOČEK (*Zeitsch. Zuckerind. Böhm.*, 1919, **43**, 572—574).—*Rhodeoseoxime*, m. p. 188—189°, is obtained in 97% yield by the action of Wohl's hydroxylamine solution on an aqueous solution of rhodose; *fucoseoxime* is similarly prepared, and has m. p. 188—189° when rapidly heated. When treated with acetic anhydride and sodium acetate, each oxime yields the same *acetylrhodeonitrile*, m. p. 177—178°, whilst, in addition, a *substance*, m. p. 115—116°, which does not appear to be an acetyl-nitrile, is obtained as by-product from rhodoseoxime. *isoRhodose*, in sharp contrast to rhamnose, rhodose, and fucose, does not yield a sparingly soluble oxime. H. W.

**Action of Braun's Dihydrazine on certain Methyl-pentoses.** E. VOTOČEK (*Zeitsch. Zuckerind. Böhm.*, 1919, **43**, 574—577).—It has been shown by von Braun that diphenyl-

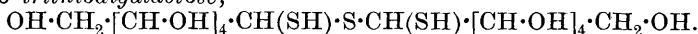
methanedimethylhydrazine does not react with ketonic sugars, but yields hydrazones with arabinose, rhamnose, galactose, and mannose, but not with xylose or dextrose; in a private communication to the authors he has suggested that this difference in behaviour of aldoses is connected with the spatial arrangement of the hydrogen and hydroxyl groups around the three asymmetric carbon atoms adjacent to the aldehydic group, and that when these groups occupy



alternate positions (annexed formula) there is no tendency towards the formation of a hydrazone. This hypothesis has been tested and confirmed at the instances of rhodose, fucose, and isorhodose, since the former two readily give *hydrazones*, m. p. 218° and 221° (partial decomp.) respectively, whilst the last-named does not react with Braun's dihydrazine. H. W.

**Thiodisaccharides from Galactose.** WILHELM SCHNEIDER and ANNEMARIE BEUTHER (*Ber.*, 1919, **52**, [B], 2135—2149).—The observation that certain saccharoses react more readily with hydrogen sulphide in pyridine solution than does dextrose has led the authors to an extended examination of the behaviour of *d*-galactose in the hope of elucidating the constitution of the thio-derivatives.

When a solution of *d*-galactose in ice-cold pyridine is repeatedly saturated with dry hydrogen sulphide with exclusion of air and the product is worked up as already described in the case of dextrose (A., 1916, i, 791) and converted into the silver salt, a product is obtained which contains, as in the case of the dextrose derivative, more than one atom of sulphur for each atom of silver. During the course of the initial action, however, a crystalline *precipitate* is observed to separate, which has the composition  $\text{C}_{12}\text{H}_{26}\text{O}_{10}\text{S}_3\cdot 3\text{C}_5\text{H}_5\text{N}$ , and readily passes by loss of pyridine into *trithiodigalactose*,



The latter melts somewhat indefinitely between 139° and 142°, and is readily decomposed even by solution in water or aqueous pyridine. Protracted boiling with water converts it into galactose. The specific rotation could not be accurately determined on account of its instability; solutions in aqueous pyridine are initially laevorotatory, but rapidly change in sign, probably owing to a more or less complete hydrolysis of trithiogalactose to galactose. When an aqueous solution is treated with silver nitrate, silver sulphide is immediately precipitated, so that the isolation of a silver salt is impossible. Confirmation of the formula attributed to trithiodigalactose is found in its conversion into a *dodeca-acetyl* derivative, leaflets, m. p. 157°,  $[\alpha]_D^{20} + 24\cdot 8^\circ$ , in acetylene tetrachloride solution.

The quantity of the crystalline compound which separates only corresponds with a small amount of the original material; further precipitations were therefore effected by the regulated addition of ether to the filtrate, whereby a *product*, needles, m. p. 183—184°, which has also the composition of a trithiodisaccharose, was isolated;



this is possibly either an isomeride or a disulphide oxidation product of trithiodigalactose.

The isolation of a trithiodisaccharose affords an obvious explanation of the high sulphur content of the thio-sugars and their silver salts.

The contrast between the stability of the sulphur atom in thioisotrehalose (Schneider and Wrede, A., 1917, i, 540) and the instability of trithiodigalactose has led the authors to prepare thio- and seleno-digalactose, which are found to be perfectly stable substances; thus *octa-acetylthiodi-d-galactose*, colourless, slender needles, m. p.  $200^{\circ}$ ,  $[\alpha]_D^{19} - 5.72^{\circ}$  or  $-6.08^{\circ}$ , in acetylene tetrachloride solution, is prepared by the interaction of bromoacetylgalactose on an alcoholic solution of potassium sulphide, and is transformed by methyl-alcoholic ammonia into *thiodi-d-galactose*,  $C_{12}H_{22}O_{10}S$ , colourless, pointed needles, m. p.  $230^{\circ}$ ,  $[\alpha]_D^{20} - 41.86^{\circ}$  in aqueous solution. The latter substance closely resembles thioisotrehalose in chemical properties; with mercuric chloride solution it yields a white precipitate,  $2HgS, HgCl_2$ . Similarly, *octa-acetylselenodigalactose* crystallises in small, colourless needles, m. p.  $202^{\circ}$ ,  $[\alpha]_D^{19} - 13.4^{\circ}$  or  $-12.5^{\circ}$  in acetylene tetrachloride, and is converted by methyl-alcoholic ammonia into *selenodi-d-galactose*, slender needles grouped in clusters, m. p.  $228^{\circ}$ ,  $[\alpha]_D^{19} - 36.6^{\circ}$  or  $-37.6^{\circ}$  in aqueous solution.

H. W.

**Action of Hydrogen Sulphide on Sugars. II.** WILHELM SCHNEIDER and OTTILIE STIEHLER (*Ber.*, 1919, **52**, [B], 2131—2135).—A further study of the action of hydrogen sulphide on dextrose and other sugars in pyridine solution (compare Schneider, A., 1916, i, 791).

The proportion of sulphur which enters the dextrose molecule is found to increase with the duration of the action and with increasing concentration of hydrogen sulphide, so that it appears that the system tends towards an equilibrium between unchanged and thio-sugar, water and hydrogen sulphide. Under suitable conditions, the dextrose molecule can combine with considerably more than one atom of sulphur.

Among the hexoses, *d*-galactose, *d*-mannose, and *d*-fructose react considerably more rapidly with hydrogen sulphide than does dextrose and absorb more than one atom of sulphur for each molecule; the behaviour of *l*-rhamnose and *l*-arabinose is similar. Lactose and maltose, on the other hand, only react very slowly, whilst  $\alpha$ -methylglucoside and mannitol do not yield thio-compounds. The slight activity of penta-acetylglucose is probably due to the preliminary loss of one or more acetyl groups. The ability to yield thio-derivatives appears to depend on the presence of a reactive ketonic or aldehydic group in the molecule.

H. W.

**Action of Reducing Agents on the Chloraloses.** M. HANRIOT and ANDRÉ KLING (*Ann. Chim.*, 1919, [ix], **12**, 129—150).—When the chloraloses are heated with ammonia in solution in perfectly dry methyl alcohol in sealed tubes at  $150^{\circ}$  for four to

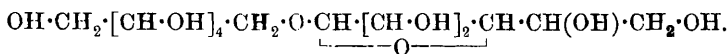
six hours, one of the three atoms of chlorine is replaced by hydrogen, giving products which the authors name dechlorochloraloses. With benzoyl chloride these compounds give dibenzoyl derivatives. Thus  $\beta$ -chloralose gives *dechloro- $\beta$ -chloralose*,  $C_8H_{12}O_6Cl_2$ , m. p. 156—157°,  $[\alpha]_D - 10.57^\circ$ , giving a *dibenzoyl* derivative;  $\alpha$ -chloralose gives *dechloro- $\alpha$ -chloralose*, m. p. 165°,  $[\alpha]_D + 9.96^\circ$ , giving a *dibenzoyl* derivative, m. p. 146°.  $\beta$ -Galactochloralose gives the compound,  $C_8H_{12}O_6Cl_2$ , occurring in two forms, one having m. p. 96°, the other m. p. 133°; both have  $[\alpha]_D - 29.20^\circ$ , and give a *dibenzoyl* derivative, m. p. 116°.  $\beta$ -Arabinochloralose gives the compound  $C_7H_{10}O_5Cl_2$ , m. p. 88—89°,  $[\alpha]_D - 19.72^\circ$ , giving a *dibenzoyl* derivative, m. p. 90.5°.

On oxidation with nitric acid dechloro- $\beta$ -chloralose gives a mixture of a lactone and an acid, from which, by the action of ammonia, *dechloro- $\beta$ -chloralamide*,  $C_7H_9O_5Cl_2 \cdot CO \cdot NH_2$ , m. p. 161—162°, is obtained. Under similar conditions dechloro- $\beta$ -galactochloralose on oxidation only yields mucic acid. Dechloro- $\beta$ -arabinochloralose yields an acid,  $C_7H_8O_6Cl_2$ , m. p. 215°.

When hydrolysed with hydrochloric acid the dechlorochloraloses simply split up, giving the sugar and dichloroacetaldehyde. The dechlorochloraloses may be more easily obtained, and with better yield, by the reduction of the corresponding chloralose with aluminium amalgam in neutral or acid aqueous alcoholic solution, or with a zinc-copper couple or zinc and sulphuric acid, or by electrolysis in acid solution. When reduced in alkaline solution, as by the action of sodium amalgam, the  $\alpha$ - and  $\beta$ -chloraloses derived from dextrose each lose two atoms of chlorine, yielding respectively *bidechlorogluco- $\alpha$ -chloralose*,  $C_8H_{13}O_6Cl$ , m. p. 168°, giving a *dibenzoyl* derivative, m. p. 149°; and *bidechlorogluco- $\beta$ -chloralose*, m. p. 166°, giving a *dibenzoyl* derivative, m. p. 146°. On oxidation, the former of these two compounds gave oxalic and saccharic acids, whilst the second gave a lactone,  $C_7H_7O_5Cl$ , isolated as its *hydrazone*,  $C_7H_7O_5Cl \cdot N_2H_4$ , m. p. 170°.

Attempts to remove the third atom of chlorine from the chloraloses by reduction were not successful. W. G.

**Catalytic Hydrogenation of Lactose.** J. B. SENDERENS (*Compt. rend.*, 1920, 170, 47—50).—A repetition of Ipatiev's work on the catalytic hydrogenation of lactose in aqueous alcoholic solution in the presence of nickel and nickel oxide (compare A., 1913, i, 10). It is now shown that if the catalyst is only slightly active, the reaction ceases when the aldehyde group is reduced to the group  $\cdot CH_2 \cdot OH$ , and the author has isolated the resulting compound, which he calls *lactositol*,



This compound has m. p. 78°,  $[\alpha]_D + 12.2^\circ$ , and crystallises with  $1H_2O$ . On hydrolysis with dilute sulphuric acid it yields sorbitol and galactose.

If in the hydrogenation a more active catalyst is used, the action

proceeds further, the acetal group being attacked, hydrolysis occurs, and the resulting products are dulcitol and sorbitol. W. G.

### Isolation of Inulin and Lævulose from Plant Sap.

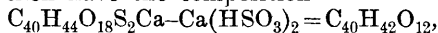
ARNOLD DANIEL (D.R.-P. 313986; from *Chem. Zentr.*, 1919, iv, 665).—The process depends on the addition of strongly alkaline substances in the warm, whereby the harmful non-inulin substances are partly precipitated and partly converted into a harmless form; the concentration of the alkali is to be so chosen that a further precipitation does not occur on treatment of the sap. The preparation of inulin from dahlia tubers by means of alkali hydroxides, or carbonates, or alkaline earths is described. Pure inulin may also be converted into pure lævulose and other degradation products of inulin, such as caramel and dextrin.

H. W.

### Chemical Structure of the Lignin of Spruce Wood.

PETER KLASON (*Arkiv Kem. Min. Geol.*, 1917, 6, No. 15, 1—21).—Spruce wood has previously been shown to consist approximately of: 50% cellulose, 16% other carbohydrates, 30% lignin, and 4% of other substances. Since the "other carbohydrates" have become of great practical importance, the name "lignosans" is suggested for them.

The composition of lignin has previously been derived from a study of barium lignosulphonate and found to be  $C_{40}H_{40}O_{11}$  (compare A., 1908, i, 717, the composition then being wrongly given as  $C_{40}H_{42}O_{11}$ ). Calcium lignosulphonate,  $C_{40}H_{44}O_{18}S_2Ca$ , has now been prepared; it apparently contains one molecule more water than the barium salt, and gives a cryoscopic molecular weight of 1628—1753, so that it forms double molecules in aqueous solution. Lignin would then have the composition



that is, it results from the condensation of 1 mol. of coniferyl alcohol and 3 mols. of hydroxyconiferyl alcohol with the loss of 3 mols. of water. (This composition is apparently taken as preferable to that obtained from the barium salt.) Naphthylamine lignosulphonate is readily obtained as a yellow, sandy powder by precipitating a solution of the calcium salt with naphthylamine hydrochloride.

When the mother liquors, from which the above calcium salt has been precipitated, are heated with naphthylamine hydrochloride, a naphthylamine lignosulphonate,  $C_{59}H_{60}O_{14}S_2N_3$ , different from the above, is precipitated. This can be considered as made up of: 1 mol. of coniferyl alcohol, 1 mol. of hydroxyconiferyl alcohol, 1 mol. of caffeic acid, 2 mols. of  $H_2SO_3$ , and 3 mols. of naphthylamine, the condensation of the first three components taking place with the loss of 3 molecules of water. The lignin forming the basis of this salt would thus have the formula  $C_{29}H_{26}O_8$ , and contain two methoxy-groups. Assuming that the lignin of wood is made up of an equal number of molecules of the two above lignins, its formula would be  $C_{69}H_{68}O_{20}$ , with six methoxy-groups, and such a composition agrees very well with analytical data.

It is suggested that the condensations above mentioned take place between the hydroxyl of an allyl alcohol group and the phenolic hydroxyl in another molecule, and so on, lignin thus being built up on the same principle that holds for polysaccharides and albumins.

The reason for including caffeic acid in the building up of the lignin  $C_{29}H_{26}O_8$  is that an acid residue must be present to account for the third molecule of naphthylamine in the salt, the other two molecules being bound by the sulphurous acid. Plant products are often substituted benzene derivatives, the first position being occupied by allyl alcohol or acrylic acid residues, whilst the positions 3, 4, and 5 are occupied by hydroxyl or methoxyl groups; caffeic acid is such a derivative.

The results obtained by the dry distillation of wood are in agreement with the above deductions, and all known facts agree with the assumption that lignin from spruce wood results from the condensation of methylated hydroxycinnamyl alcohols or the corresponding aldehydes and acids, which are substituted similarly to protocatechuic acid.

Combinations of lignin and sulphite have the character of tannins, and lignin can be considered to be an insoluble tannin.

Investigation of the molecular weight of the above-mentioned calcium lignosulphonate by the ebullioscopic method gives the value 982 (theory, 916), so that at the boiling point it is not associated; the potassium salt gave similar results. Lignin prepared from spruce wood by digesting it with alcoholic sulphuric acid and removing the fat and resin with light petroleum gave a molecular weight of 650 in glacial acetic acid, as compared with the theoretical value 714 for  $C_{40}H_{42}O_{12}$ , that is, in agreement with the formula for the lignosulphonate.

Experiments on the behaviour of coniferin and coniferyl alcohol towards acid sulphites gave results in agreement with the assumption that lignin contains aromatic nuclei of the same structure as coniferyl alcohol, together with side-chains of the same constitution as allyl alcohol. The lignin reactions (compare A., 1908, i, 717), which are also given by calcium lignosulphonate after treatment with alkali, point to the same conclusion.

The final conclusion of the author is that lignin in wood is built up from pentoses, as the following equation, which gives dihydroxycinnamyl alcohol, indicates:  $2C_5H_{10}O_5 = C_9H_{10}O_3 + 5H_2O + CO_2$ . The methylation of the phenolic groups may be brought about by formaldehyde,  $R \cdot OH + CH_2O = R \cdot OCH_3 + O$ , the oxygen liberated then changing  $RH$  into  $R \cdot OH$ , and also oxidising allyl alcohol complexes into the corresponding aldehydes and acids, thus giving the complexes shown to be present in lignin.

T. S. P.

### Preparation of Hexamethylenetetramine Dinitrate.

ZENTRALSTELLE FÜR WISSENSCHAFTLICH-TECHNISCHE UNTERSUCHUNGEN (D.R.-P. 298412; from *Chem. Zentr.*, 1919, iv, 498—499).—Solid hexamethylenetetramine is added, preferably with cooling, to

dilute aqueous nitric acid, which may contain sulphuric acid. Separation of the salt occurs so completely (about 95% of that theoretically possible) that the reaction may be applied immediately to the precipitation of nitric acid from its aqueous solution. H. W.

**Reduction of Methylene-blue by Glycine.** FRIEDRICH HASSE (*Biochem. Zeitsch.*, 1919, **98**, 159—177).—Glycine reduces methylene blue in alkaline solution. Other amino-acids do not give this reaction. Quantitative estimations show that acetaldehyde and dextrose give a weaker, creatine, catechol, and resorcinol an equal, and glucosamine and to a much greater extent adrenaline and quinol a higher reduction than glycine. These observations are discussed in relation to the Strecker-Traube reactions.

S. S. Z.

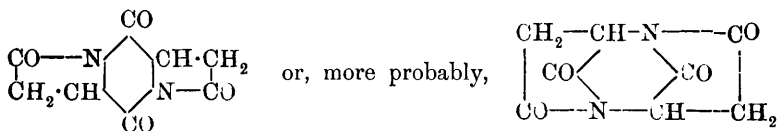
**Calcium Haloid Salts of Carbamide and Asparagine.** YUZURU OKUDA and KIYOSHI FUJIWAKA (*J. Tokyo Chem. Soc.*, 1919, **40**, 404—412).—Carbamide and asparagine form double compounds with calcium haloids, which are easily crystallised. Thus the compound,  $\text{CaI}_2 \cdot 6\text{CO}(\text{NH}_2)_2$ , m. p. 168—169°, hexagonal plates having a bitter taste, is obtained by passing hydrogen sulphide into a mixture of powdered calcium carbonate, iodine, and a little water until the iodine has dissolved, removing the excess of carbonate, and adding carbamide to the filtrate, which is then made slightly alkaline with lime-water; the crystals are obtained by concentrating the solution, and are recrystallised from water or alcohol. Other compounds described are:  $\text{CaBr}_2 \cdot 6\text{CO}(\text{NH}_2)_2$ , m. p. 146°, hexagonal plates;  $\text{CaCl}_2 \cdot 4\text{CO}(\text{NH}_2)_2$ , hygroscopic, hexagonal crystals;  $\text{CaI}_2 \cdot \text{C}_4\text{H}_8\text{O}_3\text{N}_2 \cdot 4\text{H}_2\text{O}$ , m. p. 136°;  $\text{CaBr}_2 \cdot \text{C}_4\text{H}_8\text{O}_3\text{N}_2 \cdot 4\text{H}_2\text{O}$ ; and  $\text{CaCl}_2 \cdot \text{C}_4\text{H}_8\text{O}_3\text{N}_2 \cdot 4\text{H}_2\text{O}$ , m. p. 67°, hygroscopic, columnar crystals.

CHEMICAL ABSTRACTS.

**Transformation of Asparagine into the Dipeptide of Aspartic Acid.** C. RAVENNA and G. BOSINELLI (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 113—117).—When ordinary *l*-asparagine is subjected to prolonged boiling in aqueous solution, it undergoes partial racemisation (compare Fringsheim, A., 1910, i, 303; ii, 437). From the inactive asparagine separable from the solution by crystallisation, the *d*-isomeride may be obtained pure by dissolving a little magnesium sulphate and potassium and calcium hydrogen phosphates in the 2% aqueous solution and leaving the latter exposed for fifteen days to the air at the ordinary temperature; the mould which develops on the liquid rapidly attacks the *l*-asparagine, and the *d*-asparagine may afterwards be crystallised out.

The mother liquors from the inactive asparagine yield no further crystals, but are found to contain the dipeptide of aspartic acid (asparagylaspartic acid) (compare Fischer and Koenigs, A., 1907, i, 486),  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ . The latter may be purified by heating it in an open vessel for some hours

at 210°, this treatment converting it into *diketopiperazinediacetic anhydride*,



which neither melts nor decomposes at 320°; by baryta water in the cold this anhydride is transformed into asparagylaspartic acid.

In view of the widespread occurrence of asparagine in plants and the importance of the polypeptides in relation to the synthesis of proteins, it seems possible that the ready formation of the dipeptide of aspartic acid from asparagine may play a part in vegetable metabolism.

T. H. P.

**Transformation of Ammonium Malate into the Dipeptide of Aspartic Acid.** C. RAVENNA and G. BOSINELLI (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 137—139).—The composition and characters of diketopiperazinediacetic anhydride (compare preceding abstract) indicate the identity of this compound with that obtained by Dessaignes (Beilstein, 3rd edition, I, 1389) by heating ammonium hydrogen malate, and described in the older literature as fumarimide. The conversion of the latter compound into the dipeptide of aspartic acid by the action of baryta solution in the cold confirms the identity.

T. H. P.

**Chloroacetates of S-Alkylthiocarbamides.** JOHN TAYLOR (T., 1920, 117, 4—11).

**Equilibrium Conditions in the Bucher Process for the Fixation of Nitrogen.** J. H. FERGUSON and P. D. V. MANNING (*J. Ind. Eng. Chem.*, 1919, **11**, 946—950).—In Bucher's process for the fixation of nitrogen the main reaction is represented by the equation  $2\text{Na}_2\text{CO}_3 + 4\text{C} + \text{N}_2 \rightleftharpoons 2\text{NaCN} + 3\text{CO}$ , the iron apparently acting only as catalyst. In order to ascertain the empirical relationships which may be taken as representing the probable conditions of equilibrium in practice, a stream of gas of varying composition was passed over the charge, which was heated in an iron boat and the amounts of carbonate converted into cyanide at the equilibrium points were estimated. It was found that the iron boat was not affected in experiments at 950° to 1000° in which the gas contained up to 80% of carbon monoxide. Curves were plotted showing the percentage formation of cyanide in relation to the proportion of carbon monoxide in the initial gas. The results indicated that the temperature has relatively little influence on the conversion when the gas contains little carbon monoxide, but would have much more influence in the case of gas, such as producer gas, containing, say, 30% of carbon monoxide. At 1000° it is possible to convert up to about 60% of the alkali carbonate by means of pro-

ducer gas, and the yield would be increased by the use of a higher temperature. The amount of conversion decreases with the rise in the proportion of carbon monoxide in the initial gas, and in the case of gas containing 60% of carbon monoxide only half of the carbonate is converted. The results also indicated that the initial reduction of the sodium carbonate to sodium is the controlling factor in the Bucher process, and that the effect of the carbon at this stage may be to maintain the pressure of the carbon dioxide below that of the dissociation pressure of the carbonate. This view received support from the results obtained by plotting the amounts of carbonate converted into cyanide in relation to carbon dioxide instead of carbon monoxide. [See, also, *J. Soc. Chem. Ind.*, 1920, 17A.] C. A. M.

**Action of Mercuric Cyanide on Metallic Salts.** LILANANDA GUPTA (T., 1920, 117, 67—73).

**Effect of Pressure, and of Dissolved Air and Water on the Melting Point of Benzene.** THEODORE W. RICHARDS, EMMETT K. CARVER, and WALTER C. SCHUMB (*J. Amer. Chem. Soc.*, 1919, 41, 2019—2028).—The freezing point of benzene and the effect of dissolved air and water on this quantity have been experimentally investigated. It is shown that benzene saturated with air under atmospheric pressure melts  $0.003^{\circ}$  below the true triple point. Benzene thus saturated has its freezing point but little altered by change of pressure. There appears to be no large amount of supersaturation. The effect of pressure in the absence of dissolved air is shown to alter the freezing point  $0.029^{\circ}$  per atmosphere. Saturation with water lowers the freezing point of benzene  $0.095^{\circ}$ . The true freezing point of benzene saturated with air is probably not far from  $5.493^{\circ}$  and the true triple point not far from  $5.496^{\circ}$ . J. F. S.

**The Nitrotoluenes. III. Binary Systems of the Components: *p*-Nitrotoluene, 2:4-Dinitrotoluene, and 2:4:6-Trinitrotoluene.** JAMES M. BELL and CHARLES H. HERTY, Jun. (*J. Ind. Eng. Chem.*, 1919, 11, 1124—1128. Compare this vol., i, 22, 23).—The melting points of two-component systems of three of the principal nitration products of toluene have been determined by the cooling-curve method, and the complete results plotted in curves. The term "melting point" is defined as the temperature at which crystals first appear, and in determining it the question of super-cooling has to be taken into consideration, whilst the eutectic point is the temperature at which there is equilibrium between the solids and melted mass. The probable values found for the melting points were: For *p*-nitrotoluene (*MNT*),  $51.5^{\circ}$ ; 2:4-dinitrotoluene (*DNT*),  $69.6^{\circ}$ ; and 2:4:6-trinitrotoluene (*TNT*),  $80.35^{\circ}$ , in each case with a + or - error of  $0.3^{\circ}$ . In the binary system *MNT-TNT* the eutectic points were  $33.85-33.95^{\circ}$ ; in the system *DNT-TNT*,  $45.4-45.6^{\circ}$ ; and in the system *MNT-DNT*,  $26.44-26.54^{\circ}$ . In no instance did the freez-

ing-point curves intersect at other than the eutectic temperature points, and the conclusions of Giua (A., 1914, i, 817) as to the existence of molecular compounds in these three cases were therefore not supported by these results. C. A. M.

**The Nitrotoluenes. IV. The Three-component System: *p*-Nitrotoluene, 2:4-Dinitrotoluene, and 2:4:6-Trinitrotoluene.** JAMES M. BELL and CHARLES H. HERTY, Jun. (*J. Ind. Eng. Chem.*, 1919, 11, 1128—1130).—The freezing points of mixtures of these compounds have been determined and plotted in the conventional triangular diagrams, the primary freezing point being the temperature at which the first solid separated, the second that at which the second solid separated, and the eutectic point that at which all three solids were in equilibrium with the melted mass. The diagram thus consisted of three fields separated by three boundary curves, which intersected at the ternary eutectic point. No evidence was obtained pointing to the existence of binary molecular compounds as claimed by Giua (see preceding abstract). By a method of interpolation both the composition and temperature of points on the boundary curves may be found, and in this way it is possible to identify the composition of a mixture of the three compounds from the determination of the freezing points. C. A. M.

***p*-Cymene. III. Preparation of 2-Chloro-5:6-dinitro-*p*-cymene.** H. A. LUBS and R. C. YOUNG (*J. Ind. Eng. Chem.*, 1919, 11, 1130—1133. Compare A., 1918, i, 339; 1919, i, 398).—The chief product formed in the nitration of 2-chloro-*p*-cymene is 2-chloro-5:6-dinitro-*p*-cymene, whilst an isomeric compound also appears to be formed. Another chlorodinitro-compound (m. p. 90—91°) containing less carbon than chlorodinitrocymene is also formed in small quantity, together with a substance of unknown composition, possibly a chloroterephthalic acid. C. A. M.

**4-Chlorobenzene-1:3-disulphonic Acid and its Transformation into the Symmetrical Compound.** S. C. J. OLIVIER (*Rec. trav. chim.*, 1919, 38, 351—355).—4-Chlorobenzene-1:3-disulphonic acid gives a *potassium* salt,  $C_6H_3Cl(SO_3K)_2 \cdot H_2O$ , a *barium* salt,  $C_6H_3Cl(SO_3)_2Ba \cdot 4H_2O$ , and a *dichloride*,  $C_6H_3Cl(SO_2Cl)_2$ ,  
m. p. 90·5°.

When the anhydrous barium salt is heated with sulphuric acid, containing some sulphur trioxide, at 300° for five hours it is partly converted into 5-chlorobenzene-1:3-disulphonic acid. W. G.

**The Structure of the Chlorobenzenedisulphonic Acid prepared according to D.R.-P. 260563.** S. C. J. OLIVIER (*Rec. trav. chim.*, 1919, 38, 356—357).—By preparation and identification of its acid chloride it is shown that the acid obtained by the sulphonation of *p*-chlorobenzenesulphonyl chloride by the method of Meister, Lucius, and Brüning (D.R.-P. 260563) is 4-chlorobenzene-1:3-disulphonic acid. W. G.



**Iodination of Aromatic Amines by means of Iodine and Persulphate.** K. ELBS and H. VOLK (*J. pr. Chem.*, 1919, [ii], 99, 269—275. Compare A., 1913, i, 841).—The success of this method when applied to aromatic amines and their acyl derivatives is very limited. The yields of 2-iodo-*p*-nitroaniline (*acetyl* derivative, needles, m. p. 128—130°) and 2:4-di-iodo-*o*-nitroaniline were good; of 2-iodo-*p*-toluidine and 2-iodosulphanilic acid, moderate; of 2:4-di-iodoaniline (accompanied by *p*-iodoaniline), *p*-iodoacetanilide, and 3-iodo-*p*-bromoaniline, poor. Indefinite products were obtained from *m*-xylidine, dimethylaniline, diphenylamine and its acetyl derivative, *p*-chloroaniline, *m*-bromoaniline, and *m*-nitroaniline, as well as from anisidine and phenacetin, although unpublished experiments with anisole and phenetole had given excellent results. Tribenzylamine was oxidised to benzaldehyde, and hexamethylenetetramine gave its additive di-iodide.

Except in the case of acetanilide, the acetic acid used in the earlier experiments was replaced by concentrated hydrochloric acid.

J. K.

**A New Modification of 3:4-Dinitromethylaniline.** HERBERT SWANN (*T.*, 1920, 117, 1—4).

**Acylvanillylamides.** E. K. NELSON (*J. Amer. Chem. Soc.*, 1919, 41, 2121—2130).—Having shown capsaicin to be decenovanillylamide (compare A., 1919, i, 543), the author has prepared a number of acylvanillylamides and approximately determined their pungency. These amides are readily prepared by action on vanillylamine with the requisite acyl chloride. *Acetovanillylamide* has m. p. 84—85° (corr.);  $n_D$  1.550;  $n_B$  1.585;  $n_F$  1.685; *propiovanillylamide* has m. p. 108—110° (corr.);  $n_D$  1.495;  $n_B$  1.635;  $n_F$  1.680; *n-butyrovanillylamide* has m. p. 68—70° (corr.);  $n_D$  1.515;  $n_B$  1.580;  $n_F$  1.655; *isobutyrovanillylamide* has m. p. 118—120°;  $n_D$  1.465;  $n_B$  1.633;  $n_F$  1.635; *n-hexovanillylamide* could not be obtained crystalline; *n-heptovanillylamide* has m. p. 59—61° (corr.);  $n_D$  1.515;  $n_B$  1.595;  $n_F$  1.625; *n-octovanillylamide* has m. p. 41—43° (corr.);  $n_D$  1.56;  $n_F$  1.57; *n-nonovanillylamide* has m. p. 52°;  $n_D$  1.57;  $n_F$  1.59; *n-decovanillylamide* has m. p. 59—60°;  $n_D$  1.545;  $n_B$  1.555;  $n_F$  1.620; *n-undecovanillylamide* has m. p. 54—56°;  $n_D$  1.515;  $n_B$  1.540;  $n_F$  1.615; *n-dodecovanillylamide* has m. p. 60—61° (corr.);  $n_D$  1.52;  $n_B$  1.540;  $n_F$  1.60; *crotonovanillylamide* has m. p. 119—120° (corr.);  $n_D$  1.515;  $n_B$  1.605;  $n_F$  1.735; *undecenovanillylamide* has m. p. 53—55° (corr.);  $n_D$  1.55;  $n_B$  1.60;  $n_F$  1.63; *benzovanillylamide* has m. p. 140—142°;  $n_D$  1.590;  $n_B$  1.675;  $n_F$  1.695.

Below the *n*-hexoamide these substances have little or no pungency, but above this member the pungency increases rapidly with rise in molecular weight to the nonoamide and then diminishes again.

W. G.

**N-Methylvinylaniline.** JULIUS VON BRAUN and GEORG KIRSCHBAUM (*Ber.*, 1919, 52, [B], 2261—2265).—The substance is mainly of interest because it represents the first amine to be investi-

gated which contains the vinyl group directly united to the nitrogen atom.

Methyl- $\beta$ -bromoethylaniline is converted by trimethylamine into the quaternary bromide,  $\text{NMePh} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_3\text{Br}$ , the bromine atom of which is not removed by protracted boiling with 51% potassium hydroxide solution; the corresponding quaternary base may, however, be obtained by the action of silver oxide, and, when heated under diminished pressure, yields *methylvinylaniline*; the success of the operation is dependent on the purity of the bromide. The freshly distilled base forms a colourless liquid with a sharp odour resembling that of formaldehyde or acetaldehyde. It has  $D_4^{17.5}$  0.9887. It differs from other anilines and bases in its instability and susceptibility to change; when preserved, even with exclusion of light, it gradually becomes more viscous; after 48 hours it has  $D_4^{17.5}$  1.0144, after 96 hours  $D_4^{17.5}$  1.0408, whilst after 144 hours it is too viscous to allow determination of density. When distilled, it boils mainly at  $98-99^\circ/16$  mm., but about one-third of the base is converted into a dark red, viscous mass, probably by the alkali of the glass. A further remarkable property is the ease with which the vinyl group is removed in the form of acetaldehyde by hydrolysing agents, the reaction occurring even with boiling water. For this reason, it has not been found possible to isolate pure salts or derivatives of the base.

The properties of methylvinylaniline throw doubt on the probability of the presence of the vinyl group attached to nitrogen in morphine, as has been postulated by Wieland and Kappelmeier.

H. W.

**The Nitro-derivatives of Diphenylamine.** M. C. F. VAN DUIN and B. C. ROETERS VAN LENNÉP (*Rec. trav. chim.*, 1919, **38**, 358—368).—An endeavour to determine the position of the last two nitro-groups in 2:4:6:3':?:?-hexanitrodiphenylamine, formed by nitrating 2:4:6:3'-tetranitrodiphenylamine in the cold (compare Austen, this Journ., 1875, 165).

2:4:6:2':4'-Pentanitrodiphenylamine, m. p.  $196-197^\circ$  (corr.), is easily prepared by saturating nitric acid ( $D$  1.49) with picrylaniline at a temperature not exceeding  $25^\circ$ .

2:4:6:2':4':6'-Hexanitrodiphenylamine may be prepared by nitrating picrylaniline in a nitric-sulphuric acid mixture or by nitrating pentanitrodiphenylamine at  $70^\circ$ . It has m. p.  $249^\circ$  (decomp.).

2:4:6:2'(?):3':4'-Hexanitrodiphenylamine, m. p.  $273-274^\circ$ , is obtained by nitrating the 2:4:6:3'-tetranitro-compound in a nitric-sulphuric acid mixture at the ordinary temperature. The nitro-group in the position 3' is very mobile; ammonia and the amines react immediately with it at the ordinary temperature. Thus dimethylamine gives *pentanitrodimethylaminodiphenylamine*, m. p.  $249^\circ$  (corr.).

2:4:6:3':4'-Pentanitrodiphenylamine, m. p.  $232^\circ$  (corr.), may be prepared by heating together picryl chloride and 3:4-dinitroaniline in a sealed tube at  $140^\circ$  for eight hours, and this may be

converted into the hexanitro-derivative, m. p. 273—274°, given above, thus establishing the position of the nitro-group at 4'.

In an endeavour to establish the position of the sixth nitro-group, 3:4:6-trinitrodimethylaniline was heated in alcoholic solution with aniline in a sealed tube at 120°, the product being 4:6-dinitro-3-anilindimethylaniline, m. p. 143° (corr.). This was then nitrated, but, instead of the required pentanitrodimethylaminodiphenylamine, as described above, being obtained, the product was 2:4:6:2':4'-pentanitro-5-methylnitroaminodiphenylamine, m. p. 224—225° (corr.), which may also be prepared from 3-anilino-2:4:6-trinitrophenylmethylnitroamine, the intermediate product being 2:4:6:2'-tetranitro-5-methylnitroaminodiphenylamine, m. p. 200° (corr.).

By the action of *p*-nitroaniline on tetranitrophenylmethylnitroamine in boiling benzene solution, there is obtained a mixture of a compound, m. p. 235° (corr.), and 2:4:6:4'-tetranitro-5-methylnitroaminodiphenylamine, m. p. 200°. W. G.

**History of the Discovery of Oxonium Salts from Phenol Ethers.** F. KEHRMANN (*Ber.*, 1919, 52, [B], 2119).—The recent publication of Meyer and Gottlieb-Billroth (this vol., i, 37) on the action of nitric acid on phenol ethers leads the author to point out that the oxonium compound from thymol ethyl ether has been studied by Kehrmann and Messenger (*Ber.*, 1901, 34, 1626), and its constitution has been elucidated by Decker and Solonina (*A.*, 1902, i, 767). H. W.

**Preparation of *p*-Phenetolecarbamide.** J. D. RIEDEL (D.R.-P. 313965; from *Chem. Zentr.*, 1919, iv, 738).—Solutions of alkali cyanides are treated successively with alkaline oxidising agents and phenetidine hydrochloride; *p*-phenetolecarbamide separates immediately in good yield and in a highly pure condition. Sodium hypochlorite or sodium peroxide is cited as oxidising agent. H. W.

**Preparation of Acyl Derivatives of Cholic Acid.** J. D. RIEDEL (D.R.-P. 313413; from *Chem. Zentr.*, 1919, iv, 738—739).—*o*-Acetoxybenzoyl chloride is allowed to react with cholic acid in the presence of a substance which will combine with halogen acid. The product obtained from these substances in the presence of pyridine is a colourless, crystalline powder, insoluble in water, soluble in alcohol, m. p. 120°; it is tasteless and does not cause digestive disorders. It appears to be unchanged in the stomach, but to be readily dissolved in the intestines. It combines the pharmacological action of cholic and salicylic acids, and is expected to find application in pharmacy. H. W.

**Molecular Rearrangement in the Acylation of certain Aminophenols.** L. CHAS. RAIFORD (*J. Amer. Chem. Soc.*, 1919, 41, 2068—2080).—5-Bromo-3-amino-*p*-cresol, when acetylated, yielded 5-bromo-3-acetyl-amino-*p*-tolyl acetate, m. p. 169°, which, when hydrolysed, gave 5-bromo-3-acetyl-amino-*p*-cresol, m. p. 129°.

This compound, when benzoylated, yielded 5-bromo-3-benzoylamino-*p*-tolyl acetate, m. p. 172°, molecular rearrangement thus occurring. The constitution of the latter compound was proved by hydrolysing it, when 5-bromo-3-benzoylamino-*p*-cresol, m. p. 185°, was obtained identical with that prepared by benzoylating 5-bromo-3-amino-*p*-cresol by using 1 mol. of benzoyl chloride in ethereal solution with 2 mols. of the aminophenol.

A similar series of compounds was prepared from 4:6-dibromo-2-aminophenol. On acetylation, it yielded 4:6-dibromo-2-acetylaminophenylacetate, m. p. 199°, which, when treated with aqueous sodium hydroxide, gave 4:6-dibromo-2-acetylaminophenol, m. p. 174—175° (decomp.), and this with benzoyl chloride gave 4:6-dibromo-2-benzoylamino-phenyl acetate, m. p. 195—196°. This acetate, on saponification, gave 4:6-dibromo-2-benzoylamino-phenol, m. p. 198°, identical with that obtained by benzoylating 4:6-dibromo-2-aminophenol in dry ether.

In both these cases, therefore, the diacyl derivative always had the heavier benzoyl radicle attached to nitrogen, regardless of the order in which the radicles were introduced. As this is in direct opposition to the results obtained by Ransom and Nelson (compare A., 1914, i, 269), similar experiments were conducted with aminophenol itself, and, regardless of the order of introduction of the acyl radicles, the final product was 2-benzoylamino-phenyl acetate, m. p. 135°. Thus in these cases no differences have been observed between the behaviour, in this respect, of substituted and unsubstituted aminophenols, which indicates that acid-forming substituents are not responsible for the rearrangement. W. G.

**Halogenation. XIX. The Replacement of Sulphonic Groups by Chlorine and the Preparation of Organic Chloro-derivatives.** RASIK LAL DATTA and HARAPARBUTTY KUMAR MITTER (*J. Amer. Chem. Soc.*, 1919, **41**, 2028—2038).—When chlorine is passed into an aqueous solution of a sulphonic acid, the sulphonic group is readily replaced by chlorine, with very good yields. In some cases, additional chlorination also takes place. Aromatic substances which, in addition, contain an hydroxy-group exhibit a special facility for this displacement of the sulphonic group by chlorine, and the same has also been found true of amino-compounds, such as the nitroanilines. Under these conditions, anisole- and phenetole-sulphonic acids yield tetrachloroketocyclohexadiene and some trichlorophenol. Phenolsulphonic acid gives trichlorophenol; *o*-cresol-5-sulphonic acid gives 5-chloro-*o*-cresol; *m*-cresol-6-sulphonic acid and *m*-cresol-2:6-disulphonic acid both give 2:6-dichloro-*m*-cresol; *p*-cresol-3-sulphonic acid gives a *tri-chloro-p*-cresol, m. p. 85—86°, which is either the 2:3:6- or the 3:5:6-trichloro-derivative; *p*-cresol-3:5-disulphonic acid gives 3:5-dichloro-*p*-cresol. Thymol mono- and di-sulphonic acids both give 2:5:6-trichlorothymol; carvacrol-5-sulphonic acid gives trichlorocarvacrol; orcinoldisulphonic acid gives pentachloro-orcinol [3:5-diketomethylpentachlorocyclohexane]. *o*- and *p*-Nitrophenol-sulphonic acids give, respectively, 4:6-dichloro-*o*-nitrophenol and

2:6-dichloro-*p*-nitrophenol; *o*- and *p*-nitroanilinesulphonic acids yield, respectively, 4:6-dichloro-*o*-nitroaniline and 2:6-dichloro-*p*-nitroaniline, whereas *m*-nitroanilinesulphonic acid does not give any definite product. Salicylic acid, on sulphonation and subsequent chlorination, gives 3:5-dichlorosalicylic acid. 2:4:6-Trisulpho-*m*-hydroxybenzoic acid gives the corresponding trichloro-derivative, and 3-sulpho-*p*-hydroxybenzoic acid yields 3:5-dichloro-*p*-hydroxybenzoic acid.

W. G.

**Replacement of Sulphonic Groups by Nitro-groups by means of Nitrous Gases.** RASIK LAL DATTA and PHULDEO SAHAYA VARMA (*J. Amer. Chem. Soc.*, 1919, **41**, 2039—2048).—The sulphonic acid groups in aromatic compounds may be very easily replaced by nitro-groups by means of nitrous gases. The action is generally effected in aqueous solutions, the nitrous gases being passed until saturation is reached. In the course of the action more nitro-groups frequently enter, with the formation of highly nitrated compounds. Many nitrations which cannot be brought about at all by nitric acid can be smoothly accomplished by this method. The reaction may be used for determining the constitution of nitro-compounds derived from known sulphonic acids. Aromatic compounds which are already substituted by hydroxy-groups or by halogens readily undergo replacement of the sulphonyl group by a nitro-group, in some cases more nitro-groups entering the ring in suitable positions. In the case of hydroxycarboxylic acids containing a sulphonyl group, both the sulphonyl and the carboxyl groups are replaced by nitro-groups. If, however, the compound does not already contain substituent halogens or hydroxyl groups, replacement of the sulphonyl group does not take place at all. Thus benzenesulphonic acid remains unacted on by treatment with nitrous gases.

By this method the following compounds have been prepared: 3:4-Dinitro-*o*-cresol from either *o*-cresol-3-sulphonic acid or *o*-cresol-4-sulphonic acid; 3:5-dinitro-*o*-cresol from the 3:5-disulphonic acid; 2:4:6-trinitro-*m*-cresol from either *m*-cresol-6-sulphonic acid or the 2:6-disulphonic acid; 3:5-dinitro-*p*-cresol from *p*-cresol-3-sulphonic acid; 3:5-dinitro-*o*-4-xylenol from *o*-xylenol-4-sulphonic acid; 5-nitro-*m*-4-xylenol and 2-nitro-*p*-5-xylenol from the corresponding sulphonic acids; 6-nitrothymol from thymolsulphonic acid; 2:4:6-trinitroresorcinol from either resorcinoldisulphonic acid, *m*-nitrophenolsulphonic acid, or *m*-hydroxysulphobenzoic acid; 2:4-dinitrophenol from either anisole- or phenetole-sulphonic acid; 2:4:6-trinitrophenol from the sulphonic acids of either *o*- or *p*-nitrophenol or *o*- or *p*-hydroxybenzoic acid. By direct sulphonation and subsequent treatment with nitrous gases without isolation of the sulphonic acid, 1:2:3-cresotic acid gave 3:5-dinitro-*o*-cresol; 1:3:4-cresotic acid gave 2:4:6-trinitro-*m*-cresol; 1:4:3-cresotic acid gave 3:5-dinitro-*p*-cresol; chloro-, bromo-, and iodo-benzenes gave the corresponding *p*-nitro-derivatives; phenylacetonitrile gave *p*-nitrophenylacetonitrile; and anthraquinone gave  $\beta$ -nitroanthraquinone.

W. G.

**Preparation of Tetrahydro- $\beta$ -naphthol.** GEORG SCHROETER and WALTER SCHRAUTH (D.R.-P. 299603; from *Chem. Zentr.*, 1919, iv, 618).—Tetrahydronaphthalene- $\beta$ -sulphonic acid or its salts are fused with alkali. The acid is prepared by mixing tetrahydronaphthalene with a small excess of concentrated or absolute sulphuric acid; in the latter case the hydrocarbon dissolves immediately with spontaneous warming of the solution to 80–100°, and the process is completed by warming the mixture on the water-bath. On cooling, the mixture solidifies to a mass of crystals, from which the sulphonic acid can be isolated by pressure; alternatively, the alkali salts may be obtained by neutralising the slightly diluted mixture with alkali hydroxide and cooling, or may be salted out with potassium or sodium chloride. In addition, the alkali salts are prepared by the hydrolysis of tetrahydronaphthalene- $\beta$ -sulphonyl chloride (from the hydrocarbon and chlorosulphonic acid). When fused with potassium or sodium hydroxide, either singly or together or with addition of milk of lime, tetrahydronaphthalene- $\beta$ -sulphonic acid or its alkali salts are smoothly transformed, at 230–300°, into *tetrahydro- $\beta$ -naphthol*, silky needles, m. p. 59–60°, b. p. 145–146°/13 mm., 275–276°/760 mm., which is readily soluble in alkali hydroxide, in solutions of salts of the fatty and sulfo-fatty acids, and in concentrated sulphuric acid. The soap solutions remain permanently clear when diluted with conductivity water, whilst the naphthol is again precipitated when the sulphuric acid solutions are diluted. When the sulphuric acid solution is warmed, *tetrahydro- $\beta$ -naphthol- $\alpha$ -sulphonic acid* is formed, and crystallises when a small quantity of water is added to the solution; it is converted into a *dinitrotetrahydronaphthol*, yellow prisms, m. p. 112–114°, when treated in aqueous solution with concentrated nitric acid. Tetrahydro- $\beta$ -naphthol is intended to serve by itself or as starting material in the preparation of drugs, disinfectants, tanning materials, dyes, and explosives.

H. W.

**Tautomerism of Phenols. I. Quinol.** WALTER FUCHS and BENNO EISNER (*Ber.*, 1919, 52, [B], 2281–2286).—It is found in the case of quinol that phenols can react with sodium hydrogen sulphite in their tautomeric form as unsaturated cyclic ketones.

Reaction slowly occurs when an aqueous solution of quinol and sodium hydrogen sulphite is heated at the temperature of boiling water, whereby *sodium cyclohexane-1:4-diol-1:2:4-trisulphonate*, colourless needles, is formed. The sulphonic character of the product follows from the failure to obtain more than traces of sulphur dioxide from it by the action of mineral acids. The constitution of the substance is deduced from its oxidation by permanganate to succinic, oxalic, and, possibly, malic acids. *cycloHexane-1:4-diol-1:2:4-trisulphonic acid* could not be isolated in the pure condition; the specimens obtained consisted of a colourless, unstable material, m. p. 172–175° (decomp.), after previous darkening. The sodium salt can be used as a photographic developer; the possibility of its presence in the ordinary quinol developer is discussed.

H. W.

**Primary Aromatic Alcohols.** J. ALTWEGG (U.S. Pat. 1315619).— $\beta$ -Phenylethyl alcohol, b. p.  $89^{\circ}/4$  mm., is obtained in nearly theoretical yield by adding ethylene oxide (1 mol.) to an ethereal solution of magnesium phenyl bromide (1 mol.) at  $0^{\circ}$ , maintaining the temperature below  $10^{\circ}$  during the addition, then adding dry benzene, removing the ether by distillation, adding dilute sulphuric acid after cooling, and separating the phenylethyl alcohol from the benzene by decantation.

$\beta$ -p-Tolylethyl alcohol, b. p.  $98^{\circ}/3$  mm., is similarly obtained from magnesium p-tolyl bromide.  $\beta$ -p-Methoxyphenylethyl alcohol, b. p.  $121^{\circ}/5$  mm., is prepared with the aid of toluene instead of benzene.  $\beta$ -3-Methoxy-p-tolylethyl alcohol, similarly prepared, is a colourless oil, b. p.  $129$ — $130^{\circ}/5$  mm., with a faint, aromatic odour.

## CHEMICAL ABSTRACTS.

**A New Sterol.** TAKEO Ikeguchi (*J. Biol. Chem.*, 1919, **40**, 175—182).—The author has previously described a sterol which he isolated from *Lycoperdon gemmatum* (A., 1915, i, 240). He has now obtained a similar product from other fungi, namely, *Armillaria edodes*, *Hydnum asparatum*, and *Collybia shiitake*. The crystalline sterols obtained from these sources melt at  $159$ — $160^{\circ}$ , have  $[\alpha]_D^{20} = -129.23^{\circ}$  to  $-129.55^{\circ}$ , and the formula  $C_{30}H_{48}O_2$ . They all give the same colour reactions, which differ slightly from those characteristic for cholesterol. As the author considers these crystals represent a sterol which is present in fungi generally, he proposes to call it *mycosterol*. Mycosterol inhibits the hæmolytic action of saponin, but not so powerfully as does cholesterol. It gives a crystalline compound with digitonin,  $C_{85}H_{142}O_{30}$ , m. p.  $242^{\circ}$  (decomp.). *Mycosterol acetate*,  $C_{32}H_{50}O_3$ , has m. p.  $169^{\circ}$ . Attempts to brominate failed, so that the molecule appears to be a saturated one.

It was not found possible to prepare a phenylhydrazone, so that it would appear likely that the two oxygen atoms are both present as hydroxyl groups. Only one of these is, however, acetylated by treatment with acetic anhydride, so that the other might possibly be existent as a tertiary alcohol grouping. To gain information on this point the oxidation products of the sterol were examined. On treatment with chromic acid in acetic acid solution mycosterol yielded an oxidation product,  $C_{30}H_{48}O_3$ , m. p.  $188$ — $189^{\circ}$ . Since this substance is neutral, it is concluded that a third hydroxyl group has been formed during the oxidation,  $C_{30}H_{46}(OH)_2 \rightarrow C_{30}H_{45}(OH)_3$ . Acetylation of the oxidation product confirmed this view, for a triacetate,  $C_{36}H_{54}O_6$ , needles, m. p.  $201$ — $202^{\circ}$ , was obtained.

J. C. D.

**Synthesis in the Naphthalene Nucleus.** A. MADINAVEITIA and J. PUYAL (*Anal. Fis. Quim.*, 1919, **17**, 125—129).—The synthesis of 4-methoxy- $\alpha$ -naphthylcarbinol is described. A current of dry hydrogen chloride was passed into a mixture of  $\alpha$ -naphthyl methyl ether and anhydrous hydrogen cyanide in ethyl ether solution in presence of powdered zinc chloride. The precipitate formed

gave the aldehyde,  $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{CHO}$  (1.4), on boiling with water. This is a liquid (b. p.  $210\text{--}220^\circ/25$  mm.). On treatment with aqueous potassium hydroxide a mixture of 1-methoxy-4-naphthyl-carbinol (m. p.  $35^\circ$ ) and 1-methoxy-4-naphthoic acid (m. p.  $230^\circ$ ) was obtained. 4-Methoxy- $\alpha$ -naphthyl chloromethyl ketone,  $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , is synthesised by the action of anhydrous aluminium chloride on a mixture of  $\alpha$ -naphthyl methyl ether and chloroacetyl chloride in carbon disulphide solution; it forms needles, m. p.  $70^\circ$ . The corresponding ethoxy-derivative obtained in a similar way has m. p.  $98^\circ$ , and when heated with hydrochloric acid in a sealed tube at  $120^\circ$  yields  $\alpha$ -naphthyl chloromethyl ketone, which after recrystallisation from alcohol has m. p.  $130^\circ$ .

W. S. M.

**Preparation of Ethylidene Esters.** CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 313696; from *Chem. Zentr.*, 1919, iv, 664—665).—Organic vinyl esters or mixtures of vinyl esters are heated, in the presence or absence of a catalyst, with organic or inorganic acids, under conditions in which a molecule of the acid combines with a molecule of the ester and either at the ordinary or increased pressure until the action is complete. Thus, ethylidene diacetate is obtained by boiling vinyl acetate with acetic acid in the presence of a small quantity of concentrated sulphuric acid. Vinyl benzoate, b. p.  $203^\circ$ ,  $D_{20}^{20}$  1.065, and dry hydrogen chloride yield chloroethyl benzoate, b. p.  $134^\circ/20$  mm.,  $D_{20}^{20}$  1.172. Vinyl acetate forms ethylidene acetate benzoate,  $\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{OBz}$ , with benzoic acid and chloroethyl acetate,  $\text{OAc}\cdot\text{CHClMe}$ , with hydrogen chloride. The products are generally liquid, and excellent solvents for natural and artificial resins and cellulose nitrates and acetates; they may also be used in the preparation of varnishes, films, and impregnating mixtures.

H. W.

**Physiological Formation of Adrenaline and Syntheses of Phenylserine.** F. KNOOP (*Ber.*, 1919, 52, [B], 2266—2269).—The author criticises the views which have recently been advanced by Rosenmund and Dornsaft (this vol., i, 56) on the physiological formation of adrenaline, and points out that the production of many of the intermediate substances which they postulate is not in accordance with known physiological chemical process.

[With TOTANI].—With the object of preparing *N*-methylserine,  $\alpha$ -chloro- $\beta$ -phenyl-lactic acid was added to a solution of methylamine; contrary to expectation, the product proved to be  $\beta$ -methyl-amino- $\alpha$ -hydroxy- $\beta$ -phenylpropionic acid, long prisms, decomposing completely at  $272^\circ$  after slowly darkening at  $250^\circ$ ; since the original acid contains the hydroxyl group in the  $\beta$ -position, it follows that it must have migrated to the  $\alpha$ -carbon atom probably owing to the intermediate formation of phenylglycidic acid. The constitution of the new acid is deduced from its oxidation by barium permanganate to  $\alpha$ -methylamino- $\alpha$ -phenylacetic acid, pointed prisms which sublime without melting at  $270^\circ$ . The latter acid is also obtained by the



action of methylamine on  $\alpha$ -chloro- $\beta$ -acetyl- $\beta$ -phenyl-lactic acid, short, coarse prisms, m. p. 131°. H. W.

**Alkamine Esters of Aminotoluic Acids and Similar Compounds.** E. A. WILDMAN (U.S. Pat. 1317251).— $\beta$ -Diethylaminoethyl 3-amino-*p*-toluate is obtained by reducing with tin, alcohol, and hydrochloric acid at 35° the product of reaction of  $\beta$ -diethylaminoethyl alcohol (1 mol.) and 3-nitro-*p*-toluoyl chloride (1 mol.), removing the tin with hydrogen sulphide, and precipitating the oily ester with sodium carbonate. It forms a *hydrochloride*, colourless crystals, m. p. 157—158°. The *dimethylaminoethyl ester (hydrochloride)*, m. p. 139—140° and various other alkamine esters of aminotoluic acids may be prepared similarly. They act as local anæsthetics, having but slight irritating or toxic action.

CHEMICAL ABSTRACTS.

**Trimorphism of *allocinnamic Acids*.** A. W. K. DE JONG (*Vers. Akad. Wetensch. Amsterdam*, 1919, 27, 1219—1231).—The residue obtained by evaporating a dilute solution of either of the *allocinnamic acids*, m. p. 58° and 68°, yields the acid, m. p. 42°, at the ordinary temperature, but this acid is never obtained when concentrated solutions of the former two are used at the ordinary temperature. Aqueous solutions of the acids, m. p. 58° and 68°, yield only the acid, m. p. 58°, at -10°, but yield either of the acids at -16°. Freezing experiments, with special precautions to prevent inoculation by nuclei, were also performed, and the conclusion is drawn that the three *allocinnamic acids* are trimorphous forms.

CHEMICAL ABSTRACTS.

**Anæsthetic Alkamine Esters of Alkylxyaminobenzoic [Aminoalkylxybenzoic] Acids.** E. A. WILDMAN (U.S. Pat. 1317250).—These esters, having properties similar to those of the esters described above, are prepared in an analogous manner. *Aminoethyl m-aminoanisate* is an oil which forms a *hydrochloride*, m. p. 160°.

CHEMICAL ABSTRACTS.

**Salosalicylide and the Polymeric Salicylides.** G. SCHROETER (*Ber.*, 1919, 52, [B], 2224—2237).—The salicylides, which have hitherto been described by Anschütz, in particular that obtained by crystallisation from chloroform, show a varying molecular weight, since cryoscopic determinations in phenol or nitrobenzene indicate the formula  $(C_6H_4 \begin{smallmatrix} \diagup CO \\ | \\ O \end{smallmatrix})_4$ , and ebullioscopic determinations in chloroform or nitrobenzene indicate  $(C_6H_4 \begin{smallmatrix} \diagup CO \\ | \\ O \end{smallmatrix})_2$ ; the author now describes the preparation of a salicylide which undoubtedly has the constitution  $C_6H_4 \begin{smallmatrix} \diagup CO \cdot O \\ | \quad \diagdown \\ O \cdot CO \end{smallmatrix} C_6H_4$ , and is therefore analogous to the dianthranilide obtained by Schroeter and Eisleb (*A.*, 1909, i, 575). The immediate cause of publication is the recent

communication of Anschütz (this vol., i, 48) on a new disalicylide, which in many respects appears to be identical with the author's salosalicylide, although slight discrepancies are shown in the m. p. of the two substances and of their derivatives.

Salicylosalicylic acid, in spite of the presence of the free phenolic hydroxy-group, is smoothly converted by thionyl chloride into *salicylosalicylyl chloride*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ , m. p.  $99^\circ$ , which is converted in the usual manner into the corresponding *anilide*, long needles, m. p.  $160\cdot5^\circ$ , *p-phenetidine*, m. p.  $154^\circ$ , *methyl ester*, m. p.  $88^\circ$ , and *glycine ester*, m. p.  $90\text{--}91^\circ$ ; the latter substance is readily hydrolysed, and, on further treatment with alkali, yields salicylic and salicyluric acid or *ethyl salicylurate*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , needles, m. p.  $88^\circ$ . Salosalicylide is most conveniently prepared by boiling salicylosalicylyl chloride dissolved in benzene with diethylaniline; the dried, crystalline product has m. p.  $234^\circ$  when rapidly heated, but, after crystallisation from nitrobenzene, the m. p. is constant at  $214\text{--}217^\circ$ , whilst from benzene, a product, m. p.  $204\text{--}208^\circ$ , is obtained, the cause of these variations being unexplained. Cryoscopic and ebullioscopic determinations of the molecular weight in nitrobenzene and cryoscopic determinations in phenol show the substance to have the formula  $\text{C}_{14}\text{H}_8\text{O}_4$ .

A series of comparative experiments with salosalicylide and the so-called "chloroform-salicylide" (tetrasalicylide) is described, in all of which the latter behaves as the more stable substance. Thus, salosalicylide is converted by boiling glacial acetic acid into salicylosalicylic acid, whilst "chloroform-salicylide" remains unchanged. Similarly, the former rapidly yields methyl salicylosalicylate with methyl-alcoholic hydrogen chloride, whilst the latter is unaffected. Salicylosalicylanilide and salicylosalicyl-*p*-phenetidine are immediately obtained from salosalicylide and the requisite amine, whereas "chloroform-salicylide" can be boiled for hours with aniline without suffering alteration. Methyl alcohol containing sodium methoxide converts both salicylides into methyl salicylate. Concentrated sulphuric acid, alone and also in the presence of nitrobenzene, converts salicylosalicylic acid, salosalicylide, and "chloroform-salicylide" into salicylic acid; if the action is rapidly interrupted, it is found that the free acid is most rapidly, the "chloroform-salicylide" least rapidly, affected. Acetic anhydride and sulphuric acid convert salicylosalicylic acid into acetylsalicylosalicylic acid, the same product being mainly formed from salosalicylide; "chloroform-salicylide," however, yields *acetyltetrasalicylic acid*,

$\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , m. p. about  $120^\circ$ . Concentrated nitric acid converts salosalicylide into nitrosalicylic acid; under analogous conditions, chloroform-salicylide is but little affected, but nitration occurs with a mixture

of nitric and sulphuric acids, *nitrosalicylide*,  $\left(\text{NO}_2\cdot\text{C}_6\text{H}_3\cdot\overset{\text{CO}}{\underset{\text{O}}{\text{C}}}\right)$  m. p.  $265^\circ$ , being formed. Protracted action of nitric acid on "chloroform-salicylide" in the presence of nitrobenzene leads to the formation of a *nitrotetrasalicylic acid*.

*Methyl tetrasalicylate* is obtained as an uncrystallisable, viscous, yellow mass by the action of salicylosalicylyl chloride on the sodium compound of methyl salicylosalicylate; the possible conversion of the ester into a tetrasalicylide has not yet been fully studied.

H. W.

**Phthalic Anhydride. II. The Melting Point of Pure Phthalic Anhydride. The System: Phthalic Anhydride-Phthalic Acid.** K. P. MONROE (*J. Ind. Eng. Chem.*, 1919, **11**, 1116—1119).—Pure phthalic anhydride was prepared by subliming the product obtained by the oxidation of naphthalene in a vacuum apparatus in the presence of phosphoric oxide. The melting point of the first and second sublimates agreed. Phthalic acid was estimated by a method of differential titration, in which the sample was dissolved in acetone and the solution titrated with standard normal potassium phthalate with bromophenol-blue (tetrabromophenolsulphonaphthalein) as indicator. The sublimed preparations contained less than 0.1% of phthalic acid. The melting point was determined in a double-walled glass vessel immersed in a bath of sulphuric acid, and, after fusion, the temperature was gradually lowered to the point of incipient crystallisation. The equilibrium point of crystals and liquid was  $130.84^{\circ}$ . Mixtures of phthalic anhydride and acid tested in the same apparatus gave a eutectic temperature of  $129.74^{\circ}$ . By graphical interpolation, the melting point of pure phthalic acid was indicated to be  $208^{\circ} \pm 2^{\circ}$ . [See, further, *J. Soc. Chem. Ind.*, 1920, 57A.] C. A. M.

**Phthalic Anhydride. III. The System: Naphthalene-Phthalic Anhydride.** K. P. MONROE (*J. Ind. Eng. Chem.*, 1919, **11**, 1119—1120).—The freezing points of mixtures of pure naphthalene and phthalic anhydride were determined by the method previously described (preceding abstract), the eutectic point ( $26.9^{\circ}$ ) corresponding with 29.0% of phthalic anhydride. There was no evidence of the existence of solid solutions. The freezing points on the phthalic anhydride curve were calculated by means of the formula  $C = (-T_0 T \log_{10} x) / \Delta t$ , where  $C$  is a constant,  $x$  the mol. fraction of anhydride in the mixture,  $T_0$  the freezing point of pure phthalic anhydride,  $T$  the freezing point of the mixture, and  $\Delta t = T_0 - T$ . The calculated values of  $C$  in this equation, based on the experimental values of  $T$ , averaged 1199. And since  $L = RC / 0.4343$ , where  $L$  represents the molar heat of fusion of naphthalene (4560 cal.) and  $R$  the gas constant (1.9852 cal. per degree), the molar heat of fusion of phthalic anhydride = 5480 cal. C. A. M.

**Phloroacetophenone.** KIEMUD BEHARI SEN and PRAPHULLA CHANDRA GHOSH (*T.*, 1920, **117**, 61—63).

**Reactivity of Diphenylketen with the Nitrile Group.** ADOLFO GONZÁLEZ (*Anal. Fis. Quim.*, 1919, **17**, 130—135).—Diphenylketen was mixed in sealed exhausted tubes with various

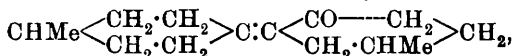
substances containing the group  $\cdot\text{C}\equiv\text{N}$ . After remaining for twenty-four or forty-eight hours at  $30^\circ$  or  $60^\circ$ , the contents of the tubes were dissolved in aqueous ether. The ether then evaporated, and the residue dissolved in alcohol. This solution of diphenylacetic acid, formed by the action of the water on the residual diphenylketen, was titrated with barium hydroxide solution. The nitriles of acetic, benzoic, and toluic acids showed only a feeble reaction with diphenylketen in the order named. Experiments with cinnamionitrile, ethylcarbamine, dimethylcyanamide, and diethylcyanamide showed that these substances also reacted to a small extent only. With cyanogen bromide, a dense liquid was obtained, after evaporation of the excess of cyanogen bromide, which yielded a yellow polymerisation product of diphenylketen.

Hydrogen cyanide and cyanogen itself did not react with diphenylketen.

W. S. M.

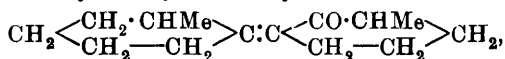
**Some New Bicyclic Ketones.** MARCEL GODCHOT and FÉLIX TABOURY (*Compt. rend.*, 1919, **169**, 1168—1171).—Using the method previously described (A., 1919, i, 447) with calcium hydride, the authors have prepared the following bicyclic ketones.

*4'-Methyl-1:1'-cyclohexylidene-3-methylcyclohexan-6-one*,



b. p.  $185^\circ/50$  mm.,  $D^{16}_D$  0.9659,  $n^{16}_D$  1.4968, gives an *oxime*, m. p.  $155^\circ$ , and, on reduction with hydrogen in the presence of platinum, using Vavon's method, gives *p-methylcyclohexyl-3-methylcyclohexan-6-one*,  $\text{C}_7\text{H}_{13} \cdot \text{C}_7\text{H}_{11}\text{O}$ , b. p.  $170\text{--}175^\circ/50$  mm.,  $D^{24}_D$  0.947,  $n^{24}_D$  1.4852, yielding an *oxime*, m. p.  $123\text{--}124^\circ$ .

*2'-Methyl-1:1'-cyclohexylidene-3-cyclohexan-2-one*,



b. p.  $175^\circ/40$  mm.,  $D^{12}_D$  0.9926,  $n^{12}_D$  1.500, gives an *oxime*, b. p.  $160\text{--}165^\circ/20$  mm., and a *semicarbazone*, m. p.  $177\text{--}178^\circ$ . On reduction by Vavon's method, it yields *2'-methyl-1:1'-cyclohexyl-3-methylcyclohexan-2-one*, b. p.  $166\text{--}169^\circ/35$  mm.,  $D^{12}_D$  0.9748,  $n^{12}_D$  1.4974, giving an *oxime* difficult to purify. Either of these ketones when reduced by sodium in absolute alcohol yields *2'-methylcyclohexyl-3-methylcyclohexan-2-ol*, b. p.  $165\text{--}168^\circ/40$  mm.,  $D^{13}_D$  0.973,  $n^{13}_D$  1.5034, giving an *allophanate*, m. p.  $223^\circ$ .

*2':4'-Dimethyl-1:1'-cyclohexylidene-3:5-dimethylcyclohexan-2-*

*one*,  $\text{CHMe} \begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array} \text{C}:\text{C} \begin{array}{c} \text{CO} \text{---} \text{CHMe} \\ \text{CH}_2 \cdot \text{CHMe} \end{array} \text{CH}_2$ , b. p.  $184\text{--}185^\circ/40$  mm.,  $D^{19}_D$  0.956,  $n^{19}_D$  1.493, gives an *oxime*, an oil, and when reduced by sodium in absolute alcohol yields *2':4'-dimethyl-1:1'-cyclohexyl-3:5-dimethylcyclohexan-2-ol*, b. p.  $188\text{--}191^\circ/40$  mm.,  $D^{16}_D$  0.945,  $n^{16}_D$  1.496, giving an *allophanate*, m. p.  $232^\circ$ . W. G.

**The Constitution of Dypnopinacone and its Derivatives.**

MAURICE DELACRE (*Ann. Chim.*, 1919, [ix], **12**, 150—178. Compare A., 1914, i, 1068; 1916, i, 679).—This paper, which should really

precede the theoretical paper previously published (compare A., 1918, i, 539), deals with the inter-relationship and preparation of the isomeric homodypnopinacones and homodypnopinacolins and their transformations. It is an elaboration of work previously published (compare A., 1896, i, 591, 662). W. G.

**Chlorothiolanthraquinones.** K. FRIES and G. SCHÜRMANN (*Ber.*, 1919, 52, [B], 2170—2181).—A continuation of previous work (A., 1912, i, 1005).

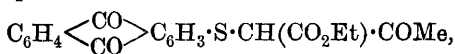
*Derivatives of 2-Thiolanthraquinone* [with K. Ross].—2-Aminoanthraquinone is diazotised in concentrated sulphuric acid solution and the diazonium sulphate is converted by potassium ethyl xanthate into *ethyl 2-anthraquinonylxanthate*, yellow needles, m. p. 151°, from which 2-thiolanthraquinone (Gattermann, A., 1912, i, 998) is obtained by the action of alcoholic potassium hydroxide solution. 2-Chlorothiolanthraquinone, yellow, prismatic crystals, m. p. 136°, is obtained by chlorination of the corresponding thiol or disulphide in chloroform solution, and is a highly reactive substance; with alcoholic potassium hydroxide solution it appears to yield a solution of potassium 2-anthraquinonesulphenate, but the corresponding acid could not be isolated. When boiled with acetone it gives 2-acetonylthiolanthraquinone,



yellow prisms, m. p. 165°, whilst with aniline in benzene or chloroform solution it forms 2-anilinothiolanthraquinone, orange needles, m. p. 171°. When a solution of the chlorothiol in chloroform is shaken with water it gives 2-anthraquinonesulphenic anhydride, small, colourless crystals, m. p. 260° (decomp.), which is also produced when the chloride is boiled with alcohol.

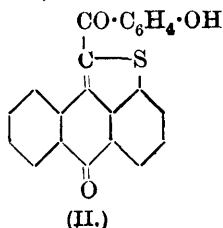
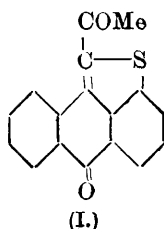
*Derivatives of 1-Thiolanthraquinone.*—Di-1-anthraquinonyl disulphide (compare Gattermann, *loc. cit.*) is most conveniently prepared by treatment of an alcoholic solution of 1-chloroanthraquinone with aqueous sodium disulphide, and is transformed into the corresponding thiol by the action of dextrose and sodium hydroxide.

1-Bromothiolanthraquinone reacts readily with ammonia, aniline, and dimethylaniline respectively, yielding the corresponding *amide*, orange needles, which do not melt below 300° and are converted by boiling acetic acid into *peri-anthraquinone-1:9-thiazole* (Gattermann, *loc. cit.*), *anilide*, shining, red needles, m. p. 210°, and *p-dimethylaminophenyl* derivative, red needles, m. p. 285°. With ethyl sodioacetoacetate, 1-bromothiolanthraquinone yields the *compound*,



yellow needles, m. p. 163°, which when boiled with mineral acid passes into the *substance* (I), yellow, prismatic crystals, m. p. 175°. Similar ring formation occurs when an alkali salt of 1-thiolanthraquinone is treated with *w*-chloro-*p*-hydroxyacetophenone, the *pro-*

*duct* (II) crystallising in golden leaflets, m. p. 258°, and yielding a red *sodium* salt. On the other hand, sodium 1-anthraquinone-



sulphenate reacts normally with *p*- and *o*-nitrobenzyl chlorides, yielding 1-anthraquinonyl *p*-nitrobenzyl sulphide, orange leaflets, m. p. 243°, and 1-anthraquinonyl *o*-nitrobenzyl sulphide, orange needles, m. p. 251°; attempts to eliminate water from these compounds with the formation of a thiophen ring were unsuccessful. Resorcinol and 1-bromothioloanthraquinone gave 1-anthraquinonyl 4-resorcyl sulphide, orange needles, m. p. 232°.

1-Anthraquinonyl phenyl sulphide, m. p. 185°, is formed by the action of benzene on 1-chlorothioloanthraquinone in the presence of aluminium chloride, and is identical with the product obtained by Gattermann (*loc. cit.*) from  $\alpha$ -nitroanthraquinone and phenyl mercaptan.

The action of ethyl sulphate on an aqueous-alcoholic solution of sodium anthraquinonesulphenate leads to the formation of 1-anthraquinonyl ethyl sulphoxide, yellow needles, m. p. 180° (decomp.), the constitution of which follows from its conversion by acetic and hydrobromic acids into 1-anthraquinonyl ethyl sulphide, m. p. 183° (Gattermann, *loc. cit.*); on the other hand, the free acid, when suspended in alcohol and treated with ethyl sulphate, is transformed into the corresponding ethyl ester, m. p. 149° (Fries, *loc. cit.*).

H. W.

**4-Aminoanthraquinone-1-sulphenic Acid.** K. FRIES and G. SCHÜRMANN (*Ber.*, 1919, 52, [B], 2182—2195).—The only sulphenic acid which has hitherto been isolated in the pure condition is 1-anthraquinonesulphenic acid (Fries, A., 1912, i, 1005); in their endeavour to isolate further examples of this class of substance the authors now describe attempts to prepare the corresponding 4-hydroxy-, 4-methoxy-, and 4-amino-compounds, which, however, are not entirely successful.

4-Bromo-1-hydroxyanthraquinone, coarse, orange-yellow needles, m. p. 197°, is prepared by the action of bromine on a hot solution of 1-hydroxyanthraquinone in glacial acetic acid in the presence of sodium acetate. (It forms a red *sodium* salt, which is sparingly soluble in water.) Under similar conditions, but with double the amount of bromine, 2:4-dibromo-1-hydroxyanthraquinone, orange needles, m. p. 235°, is produced. 4:4'-Dihydroxydi-1-anthraquinonyl disulphide, reddish-brown, flat prisms, m. p. above 300° (compare Gattermann, A., 1912, i, 998), is conveniently prepared by the

action of an aqueous solution of sodium disulphide on 1-bromo-4-hydroxyanthraquinone dissolved in alcohol, and is reduced by dextrose to 4-hydroxy-1-thiolanthraquinone, red needles, m. p. 194° (methyl thio-ether, shining, red leaflets, m. p. 217°, whereas Gattermann (*loc. cit.*) records 194°; sulphoxide of methyl thio-ether, orange-reddish leaflets, m. p. 226°). Di-4-hydroxy-1-anthraquinonyl monosulphide crystallises in red, intertwined needles, m. p. above 300°, whilst the corresponding sulphoxide forms slender, yellow needles, m. p. 287°. Di-4-hydroxy-1-anthraquinonyl disulphide is oxidised by hydrogen peroxide in sulphuric acid solution to 4-hydroxyanthraquinone-1-sulphonic acid, yellowish-brown needles, m. p. 220° (the sodium and ammonium salts are sparingly soluble in cold water and crystallise in reddish-brown leaflets with metallic glance), and by nitric acid to 3-nitro-4-hydroxyanthraquinone-1-sulphonic acid, yellow, rhombic prisms, m. p. 278°, after darkening above 255° (the sodium, ammonium, and potassium salts dissolve sparingly in cold water and form shining, yellow leaflets). 4-Hydroxyanthraquinone-1-sulphonyl chloride, golden-yellow leaflets, m. p. 246°, is obtained in place of the expected chlorothiol when a suspension of the disulphide in chloroform or glacial acetic acid is treated with chlorine; the corresponding anilide forms shining, yellow needles, m. p. 199°.

1-Bromo-4-methoxyanthraquinone, pale yellow needles, m. p. 195°, is obtained by methylation of the hydroxy-compound with methyl sulphate, and is converted by sodium disulphide into di-4-methoxy-1-anthraquinonyl disulphide, yellow needles, m. p. 285° (compare Gattermann, *loc. cit.*); the latter is not attacked by bromine, and is transformed by chlorine into a sulphonic chloride, which was not further investigated; 4-methoxy-1-anthraquinonyl methyl sulphide, orange-red needles, m. p. 187°, is prepared by reduction of the disulphide, followed by methylation of the thiol so produced.

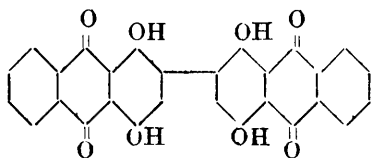
Di-4-amino-1-anthraquinonyl disulphide, m. p. above 300° (compare Gattermann, *loc. cit.*), is conveniently prepared from 4-chloro-1-aminoanthraquinone and sodium disulphide, and is readily reduced to the corresponding thiol, which could not be isolated owing to its unusual susceptibility to oxidation. It is transformed by chlorine into 3-chloro-4-aminoanthraquinone-1-sulphonyl chloride, orange-red needles, m. p. 230°, when rapidly heated after darkening above 200°; the corresponding acid forms slender, orange-yellow needles, m. p. (anhydrous) 217° (decomp.) (the ammonium salt forms red needles, m. p. about 304°, whilst the anilide, coarse, brownish-red crystals, has m. p. 210°). The sulphonic group is displaced by bromine with formation of 3-chloro-1-bromo-4-aminoanthraquinone, m. p. 217°. 4-Amino-1-chlorothiolanthraquinone is obtained in an impure condition by the action of bromine on aminoanthraquinonyl disulphide, or, preferably, by the reduction of aminoanthraquinonesulphinic acid by hydrobromic and acetic acids; it is thus obtained as an unstable hydrobromide, orange-yellow needles, which decompose





formed by the action of air on the aqueous solution of the melted mass, and not during the process of melting.

Quinizarin, according to D.R.-P. 146223, is converted by salts of weak acids into two compounds,  $C_{28}H_{14}O_8$  and  $C_{28}H_{12}O_8$ , the first of which is described as giving a soluble blue sodium salt, whilst the latter yields a bluish-violet, insoluble sodium salt. It is now shown that only the acid which forms an insoluble sodium salt is a new substance, and that it has the composition  $C_{28}H_{14}O_8$ , whilst the other product is a mixture of this acid with quinizarin. The substance is now shown to be 1:4:1':4'-*tetrahydroxy-2:2'-dianthraquinonyl* (annexed formula), since it gives 2:2'-dianthryl when distilled with zinc dust and a furan derivative when melted with zinc chloride.



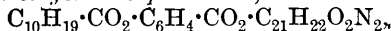
A. G. Perkin and W. H. Perkin (T., 1888, **53**, 831) have described the isolation of three substances,  $C_{28}H_{14}O_6$ ,  $C_{28}H_{14}O_7$ , and  $C_{14}H_6O_4$ , by the distillation of sodium anthraquinone-2-sulphonate; the first of these has been submitted to distillation with zinc dust, whereby anthracene and 2:2'-dianthryl are obtained, but the result does not throw any definite light on the constitution of the substance.

H. W.

### Isomeric Carvomenthols and Scission of Inactive Carvomenthol into the Optical Antipodes. I. and II.

VINCENZO PAOLINI (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 82—85, 134—137).—The author prepares pure, inactive carvomenthol by reducing carvone by means of zinc dust and sodium hydroxide, transforming the dihydrocarvone thus obtained into the isomeric carvenone by heating it with dilute sulphuric acid, and reducing the carvenone by means of sodium and alcohol. From this inactive carvomenthol, the *lævo*-isomeride may be isolated by crystallisation of the less soluble of the two carvomenthol strychnine phthalates, and conversion of this into *l*-carvomenthol hydrogen phthalate, and the latter into *l*-carvomenthol. The carvomenthol hydrogen phthalate prepared from the mother liquors of the above strychnine salt is syrupy, but, when treated with the calculated proportion of ammonia and with silver nitrate, it yields insoluble silver *d*-carvomenthol phthalate, and from this, by way of sodium *d*-carvomenthol phthalate and *d*-carvomenthol hydrogen phthalate, *d*-carvomenthol may be isolated.

*l*-Carvomenthol strychnine phthalate,



forms colourless needles, m. p. 155—156°,  $[\alpha]_D -14.76^\circ$  (in alcohol).

*l*-Carvomenthol hydrogen phthalate,  $CO_2H \cdot C_6H_4 \cdot CO_2 \cdot C_{10}H_{19}$ , forms crystals, m. p. 125°,  $[\alpha]_D -3.80^\circ$  (in alcohol).

*l*-Carvomenthol,  $C_{10}H_{19} \cdot OH$ , forms an oily, limpid liquid with a faint odour of peppermint, b. p. 218° (corr.),  $D_{15} 0.9082$ ,  $n_D^{15} 1.461$ ,  $[\alpha]_D -1.82^\circ$ .

*Silver d-carvomenthol phthalate* is obtained as a voluminous, white precipitate, and may be purified by crystallisation from absolute alcohol or by precipitation from chloroform solution by addition of alcohol and ether.

*d-Carvomenthol hydrogen phthalate* forms slender, colourless, needles, m. p.  $109^{\circ}$ ,  $[\alpha]_D + 4.62^{\circ}$  (in alcohol).

*d-Carvomenthol* has b. p.  $218^{\circ}$  (corr.),  $D^{15}_D 0.9074$ ,  $n^{15}_D 1.463$ ,  $[\alpha]_D + 1.83^{\circ}$ .  
T. H. P.

### Reduction Products of Pulegone: Pulegol. I. and II.

V. PAOLINI (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 190—192, 236—239).—Pulegol (compare Tiemann and Schmidt, A., 1897, i, 198), which previously has not been obtained free from menthol, has been prepared pure by the author.

The products formed by reducing pulegone by means of sodium and alcohol contain about 30% of a yellow resin,  $C_{20}H_{34}O_2$ , which appears to be identical with the bispulegone obtained by reducing pulegone with aluminium amalgam (compare Harries and Roeder, A., 1900, i, 183), and is of unknown constitution, although it is evidently a mixture of optical isomerides, possibly of ketonic (pinacone) character.

The mixture of alcoholic compounds separated from the reduction products of pulegone by distillation in a current of steam was esterified in the cold with phthalic anhydride (compare A., 1911, i, 730), the various hydrogen phthalates thus formed being separated by crystallisation and converted into the corresponding alcohols. In this way, *l*-menthol of peppermint oil, a solid *d*-menthol, and *l*-pulegol were isolated.

*l*-Menthol hydrogen phthalate,  $CO_2H \cdot C_6H_4 \cdot CO_2 \cdot C_{10}H_{18}$ , forms tufts of soft, white needles, m. p.  $107$ — $108^{\circ}$ ,  $[\alpha]_D - 107.5^{\circ}$ . The corresponding *l*-menthol is a crystalline solid, m. p.  $44^{\circ}$ , b. p.  $214^{\circ}$  (corr.),  $[\alpha]_D - 49.7^{\circ}$ . *l*-Menthol strychnine phthalate,

$CO_2H \cdot C_6H_4 \cdot CO_2 \cdot C_{10}H_{18} \cdot C_{21}H_{22}O_2N_2$ , forms soft, white needles, m. p.  $157$ — $158^{\circ}$ ,  $[\alpha]_D - 44.46^{\circ}$ .

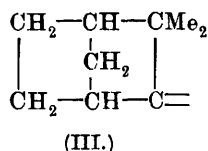
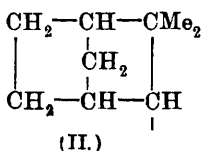
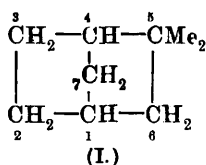
*d*-Menthol strychnine hydrogen phthalate forms crystals, m. p.  $207$ — $208^{\circ}$ ,  $[\alpha]_D - 11.7^{\circ}$ . *d*-Menthol hydrogen phthalate forms crystals, m. p.  $107$ — $108^{\circ}$ ,  $[\alpha]_D + 18.4^{\circ}$ . *d*-Menthol,  $C_{10}H_{20}O$ , is a solid and has m. p.  $88$ — $89^{\circ}$ , b. p.  $214^{\circ}$ , and  $[\alpha]_D + 21.8^{\circ}$ ; it is a saturated compound, and is possibly identical with the  $\alpha$ -pulegomenthol obtained by Haller and Martine (A., 1905, i, 533) by reducing pulegone by Sabatier's method.

*Pulegol hydrogen phthalate*,  $C_{10}H_{18}O$ , crystallises in slender, white needles, m. p.  $212^{\circ}$ ,  $[\alpha]_D - 86.8^{\circ}$ . *l*-Pulegol forms slender, white needles with a faint odour of menthol, m. p.  $46$ — $47^{\circ}$ ,  $[\alpha]_D - 54.6^{\circ}$ ; it is an unsaturated compound, and readily decolorises permanganate and bromine solution, the bromide,  $C_{10}H_{16}OBr_2$ , being a dense, colourless, oily liquid.  
T. H. P.

**Transpositions in the Camphene Series.** G. LANGLOIS (*Ann. Chim.*, 1919, [ix], **12**, 193—264).—In the first part of the

paper, a brief résumé is given of the chemistry of camphene and its derivatives. A closer study has been made of halogenation in this series, and the constitution of the monochloro- and monobromo-derivatives of camphene has been established, and a new method of synthesis for the introduction of carbon containing substituents into the side-chain has been found.

A general outline of the work is given, and the experimental work is to be published later. A new method of nomenclature is advocated for the camphene series based on the hypothetical camphenylane (formula I) and the hypothetical radicles camphenylene (formula II) and camphenylidene (formula III).

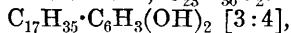


In this system, camphene becomes camphenylidene-6-methane.

W. G.

### Chemical Investigation of Various Natural Lacquers.

RIKO MAJIMA (*J. Tokyo Chem. Soc.*, 1919, **40**, 91—126. Compare A., 1908, i, 437; 1909, i, 402, 945; 1912, i, 883).—Chinese lacquer (from *Rhus vernicifera*, Dc.) is essentially the same as Japanese lacquer; both contain urushiol. Yunan lacquer (from *R. succedanea*, L. fil.), Formosan lacquer (from *Semecarpus vernicifera*), and Ivy lacquer (from *R. toxicodendron* ?) contain laccol,  $\text{C}_{23}\text{H}_{36}\text{O}_2$ , a homologue of urushiol. *Hydrolaccol*,  $\text{C}_{17}\text{H}_{35}\cdot\text{C}_6\text{H}_3(\text{OH})_2$  [2:3], m. p. 63—64°, forms a dimethyl ether, m. p. 43—44°, a mononitro-derivative, m. p. 75—76°, and dinitro-derivative, m. p. 86—87°. Burmese lacquer contains thitsiol,  $\text{C}_{23}\text{H}_{36}\text{O}_2$ . *Hydrothitsiol*,



m. p. 94—96°, forms a dimethyl ether, m. p. 56—57°, and mononitro-derivative, m. p. 75—76°; the dinitro-derivative is difficult to prepare. *Hydrothitsiol* is therefore very similar to *isohydro-urushiol*, and probably belongs to the same group. Unlike urushiol and laccol, thitsiol contains a group which is hydrogenated or ozonised only with difficulty.

Siam lacquer is probably a mixture of Yunan and Burmese lacquers. Korean lacquer is assumed to be identical with Japanese lacquer.

CHEMICAL ABSTRACTS.

### Bromination and Constitution of Caoutchouc. W. C.

SCHMITZ (*Gummi Zeit.*, 1919, **34**, 167—169, 193—195).—Purified rubber which has been "depolymerised" by heating with xylene under a pressure of 15 atmospheres forms an additive compound,  $\text{C}_{20}\text{H}_{32}\text{Br}_{10}$ , when brominated in carbon tetrachloride; this product gradually eliminates hydrogen bromide, with formation of a micro-crystalline compound,  $\text{C}_{20}\text{H}_{30}\text{Br}_8$ , which is insoluble in carbon tetra-

chloride and is quite distinct from the ordinary "caoutchouc tetrabromide." The decabromide is probably an open-chain compound, and it is uncertain whether the disruption of the cyclic caoutchouc molecule occurs during bromination or in the previous depolymerisation. In the bromination of solutions of ordinary rubber, the chemical process is complicated by colloidal phenomena which are absent in the case of the depolymerised hydrocarbon. [See also *J. Soc. Chem. Ind.*, 1920, 73A.] D. F. T.

### Preparation of Double Compounds of Caffeine with Alkali Salts of Acetylsalicylic [*o*-Acetoxybenzoic] Acid.

CHEMISCHE FABRIK J. A. WÜLFING (Brit. Pat. 136187).—*o*-Acetoxybenzoic acid (2 mols.), an alkali carbonate (1 mol.), and caffeine (1 mol.) are homogeneously mixed, and the mixture is moistened with an alcohol, ester, ketone, or chlorinated hydrocarbon of the aliphatic series to the consistency of a viscous paste, which is kneaded until a sample dissolves in water to a clear solution without the liberation of carbon dioxide. The solvent is then removed by evaporation at a low temperature, and the product, consisting of the *o*-acetoxybenzoate of caffeine and the alkali metal, is finally dried in a vacuum. G. F. M.

### Syntheses in the Cinchona Series. II. Quaternary Salts.

WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 2090—2120).—The authors have prepared a number of quaternary salts from the different cinchona alkaloids with a view to a study of their bactericidal or, more specifically, pneumococcal powers. The methochlorides, the benzyl chlorides, and the salts formed with the chloroacetyl derivatives of ammonia, the lower aliphatic amines, and benzylamine have been prepared. In the case of the chloroacetyl derivatives of the aromatic amines, the new series of salts with the alkaloids were only sparingly soluble in cold water, the other salts named above being, in general, fairly readily soluble. Solutions of all of the salts, aliphatic or aromatic, gave immediate precipitates with solutions of picric acid or potassium dichromate.

The quaternary salts of the alkaloids with the chloroacetyl derivatives of the aliphatic and aromatic amines were prepared by boiling equimolecular amounts of the components in dry acetone for five to seven hours. The following salts are described.

Cinchonine gives a *methochloride* decomposing at 270°,  $[\alpha]_D^{20} + 225.1^\circ$ ; a *benzylochloride*, m. p. 280° (decomp.),  $[\alpha]_D^{20} + 164.8^\circ$ ; an *iodoacetamide*, decomposing at about 190°; a *chloroacetamide*, m. p. 110—120° (decomp.),  $[\alpha]_D^{25} + 174.2^\circ$ .

Cinchonidine gives a *methochloride*, m. p. 232—233° (decomp.),  $[\alpha]_D^{20} - 142.7^\circ$ ; a *chloroacetamide*, m. p. about 190°,  $[\alpha]_D^{25} - 112.5^\circ$ .

Quinine gives a *methochloride*, m. p. 196—198°,  $[\alpha]_D^{20} - 211.7^\circ$ ; a *benzylochloride*, m. p. 183—188°,  $[\alpha]_D^{20} - 230.5^\circ$ ; an *iodoacetamide*, m. p. 175—180°,  $[\alpha]_D^{20} - 152.2^\circ$ ; a *chloroacetamide*, m. p. 190° (decomp.),  $[\alpha]_D^{20} - 159.6^\circ$ ; a *chloroacetanilide*, m. p. 224—225°

(decomp.),  $[\alpha]_D^{23.5} - 131.5^\circ$  (in alcohol), giving a *hydrochloride*, m. p. 204—206° (decomp.), and a *nitrate*, m. p. 201—203° (decomp.); *quinine-p-chloroacetylaminophenol*,

$C_{20}H_{24}O_2N_2 \cdot CH_2Cl \cdot CO \cdot NH \cdot C_6H_4 \cdot OH$ ,  
m. p. 205° (decomp.), *quinine-o-chloroacetylaminobenzamide*,  
 $C_{20}H_{24}O_2N_2 \cdot CH_2Cl \cdot CO \cdot NH \cdot C_6H_4 \cdot CO \cdot NH_2$ , m. p. 178—179°  
(decomp.),  $[\alpha]_D^{28} - 164.4^\circ$  (in alcohol).

Quinidine gives a *methochloride*, m. p. 250—251° (decomp.),  $[\alpha]_D^{21} + 253.1^\circ$ ; a *benzylchloride*, m. p. 180° (decomp.),  $[\alpha]_D^{21.5} + 219.9^\circ$ ; an *iodoacetamide*, m. p. 190° (decomp.),  $[\alpha]_D^{22.5} + 166.2^\circ$  (in alcohol); a *chloroacetamide*, m. p. 205° (decomp.),  $[\alpha]_D^{22} + 207.2^\circ$ ; an *iodoacetylcarbamide*, m. p. 170—175° (decomp.), and a *chloroacetylcarbamide*, m. p. 176—178° (decomp.),  $[\alpha]_D^{26.5} + 170.9^\circ$ .

Hydroquinine gives a *methiodide*, m. p. 233—235° (decomp.),  $[\alpha]_D^{20.5} - 107.6^\circ$  (in alcohol); a *methochloride*, m. p. 172—173° (decomp.),  $[\alpha]_D^{21.5} - 162.9^\circ$ ; a *benzylchloride*, m. p. 202—203.5° (decomp.),  $[\alpha]_D^{23} - 196.9^\circ$ ; an *iodoacetamide*, m. p. 185°,  $[\alpha]_D^{23.5} - 121.5^\circ$  (in alcohol); a *chloroacetamide*, m. p. 195° (decomp.),  $[\alpha]_D^{23} - 129.1^\circ$ ; a *chloroacetomethylamide*,

$C_{20}H_{26}O_2N_2 \cdot CH_2Cl \cdot CO \cdot NHMe$ ,  
m. p. 160°; a *chloroacetoethylamide*, m. p. 160°; a *chloroacetodiethylamide*; a *chloroacetodiethylamide*, m. p. 209—210° (decomp.),  $[\alpha]_D^{27.5} - 84.8^\circ$ ; a *chloroacetobenzylamide*,

$C_{20}H_{26}O_2N_2 \cdot CH_2Cl \cdot CO \cdot NH \cdot CH_2Ph$ ,  
m. p. 197—198°,  $[\alpha]_D^{23} - 42.5^\circ$ ; a *chloroacetanilide*, m. p. 210° (decomp.),  $[\alpha]_D^{24} - 95.9^\circ$  (in alcohol), giving a *hydrochloride* and a *dinitrate*; a *m-nitrochloroacetanilide*, m. p. 195—200° (decomp.); a *m-chloroacetylaminooacetanilide*, m. p. 150° (decomp.); a *p-chloroacetylaminooacetanilide*, m. p. 205°; a *p-chloroacetylaminodimethylaniline*,  $C_{20}H_{26}O_2N_2 \cdot CH_2Cl \cdot CO \cdot NH \cdot C_6H_4 \cdot NMe_2$ , m. p. 200° (decomp.),  $[\alpha]_D^{18.5} - 82.9^\circ$  (in alcohol); a *p-chloroacetylaminodiethylaniline*, m. p. 190—195°,  $[\alpha]_D^{20} - 80.5^\circ$  (in alcohol); an *o-chloroacetylaminophenol*, m. p. 185° (decomp.); a *m-chloroacetylaminophenol*, m. p. 205°,  $[\alpha]_D^{21} - 115.7^\circ$  (in alcohol), giving a *hydrochloride*, m. p. 200°; *hydroquinine-p-chloroacetylaminophenol hydrochloride*, m. p. 196—197°; *hydroquinine-4-chloroacetylaminocatechol hydrochloride*,

$C_{20}H_{26}O_2N_2 \cdot CH_2Cl \cdot CO \cdot NH \cdot C_6H_3(OH)_2 \cdot HCl$ ,  
m. p. 196—198° (decomp.); *hydroquininechloroacetyl-o-anisidine*, m. p. 185°,  $[\alpha]_D^{22} - 72.5^\circ$  (in alcohol); *hydroquininechloroacetyl-m-anisidine*, m. p. 190°,  $[\alpha]_D^{23} - 102.9^\circ$  (in alcohol), giving a *hydrochloride*, m. p. 170—171°; *hydroquininechloroacetyl-p-anisidine*, m. p. 190°,  $[\alpha]_D^{20} - 93.9^\circ$  (in alcohol), giving a *hydrochloride*, m. p. 180—184°; *hydroquininechloroacetyl-o-phenetidine*, m. p. 170—172°; *hydroquininechloroacetyl-m-phenetidine hydrochloride*, m. p. 173—174°; *hydroquininechloroacetyl-p-phenetidine*, m. p. 210°,  $[\alpha]_D^{27.5} - 89.1^\circ$  (in alcohol); *hydroquinine-4-chloroacetylaminoguaiacol*,  $C_{20}H_{26}O_2N_2 \cdot C_6H_3(OH)(OMe) \cdot NH \cdot CO \cdot CH_2Cl$ , m. p. 215° (decomp.); *hydroquinine-3:4-methylenedioxychloroacetanilide*,

$C_{20}H_{26}O_2N_2 \cdot CH_2O_2 \cdot C_6H_3 \cdot NH \cdot CO \cdot CH_2Cl$ ,

m. p. 185°; *hydroquinine-3:4-dimethoxychloroacetanilide*, m. p. 205—210° (decomp.); *hydroquinine-m-chloroacetylaminobenzene-sulphonamide*,  $C_{20}H_{26}O_2N_2 \cdot CH_2Cl \cdot CO \cdot NH \cdot C_6H_4 \cdot SO_2 \cdot NH_2$ , m. p. 200—205° (decomp.).

Hydroquinidine gives an *iodoacetamide*; a *chloroacetamide*, m. p. 210° (decomp.),  $[\alpha]_D^{25} + 179.9^\circ$ ; *hydroquinidine-p-chloroacetylaminophenol*, m. p. 285°, giving a *hydrochloride*, m. p. 245—250° (decomp.); *hydroquinidinechloroacetyl-p-anisidine*, m. p. 260—265° (decomp.), giving a *hydrochloride*, m. p. 196—200° (decomp.).

Hydrocupreine gives a *chloroacetanilide hydrochloride*, m. p. 213—214° (decomp.), and a *chloroacetyl-p-anisidine hydrochloride*, m. p. 210° (decomp.).

Ethylhydrocupreine gives a *methochloride*, m. p. 198—199°,  $[\alpha]_D^{22} - 176.7^\circ$ , and *iodoacetamide*, m. p. 185°,  $[\alpha]_D^{22} - 115.4^\circ$  (in alcohol); a *chloroacetamide*, m. p. 195°,  $[\alpha]_D^{23} - 114.8^\circ$ ; a *p-chloroacetylaminophenol*, m. p. 178—182°,  $[\alpha]_D^{22} - 71.8^\circ$  (in alcohol), giving a *hydrochloride*, m. p. 196—197°; *ethylhydrocupreinechloroacetyl-p-anisidine*, m. p. 200°,  $[\alpha]_D^{25} - 69.0^\circ$  (in alcohol), giving a *hydrochloride*, m. p. 204—205° (decomp.); *ethylhydrocupreinechloroacetyl-p-phenetidine*, m. p. 210° (decomp.),  $[\alpha]_D^{25} - 75.25^\circ$  (in alcohol), giving a *hydrochloride*, m. p. 208° (decomp.).

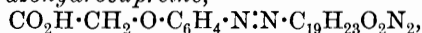
Most of the melting points given above are only approximate, as the substances turn to jellies long before they become fluid.

W. G.

**Synthesis in the Cinchona Series. III. Azo-dyes derived from Hydrocupreine and Hydrocupreidine.** MICHAEL HEIDELBERGER and WALTER A. JACOBS (*J. Amer. Chem. Soc.*, 1919, **41**, 2131—2147).—Both hydrocupreine and hydrocupreidine behave in a normal manner as phenolic compounds, and yield well-defined azo-dyes with diazotised aromatic amines, and the authors assume that position 5 in the quinoline nucleus is the place of entrance of the azo-group (compare Giemsa and Halberkann, A., 1919, i, 342). In general, the benzeneazo- and tolueneazo-dyes, as well as those with *m*-substituents in the benzene ring, dye silk various shades of orange. *o*- and *p*-Alkoxy-groups deepen these colours towards the red, whilst the dyes from the naphthylamines dye silk a deep rose colour. These substances have the property of dyeing unmordanted cotton. Many of the substances described below are highly bactericidal *in vitro*. The following azo-dyes have been prepared:

*Benzeneazohydrocupreine*, m. p. 130°, giving a *dihydrochloride*, m. p. 181—183° (decomp.); *o-tolueneazohydrocupreine*, m. p. 110—130° (decomp.); *m-tolueneazohydrocupreine*, m. p. 125—130°, giving a *dihydrochloride*, m. p. 195° (decomp.); *p-tolueneazohydrocupreine*, m. p. 202—205°;  *$\alpha$ -naphthaleneazohydrocupreine*, m. p. 146—149° (decomp.);  *$\beta$ -naphthaleneazohydrocupreine*, m. p. 240—244° (decomp.); *dibenzene-p-bisazohydrocupreine*, m. p. 204° (decomp.); *m-nitrobenzeneazohydrocupreine*, m. p. 150.5—151.5°; *p-nitrobenzeneazohydrocupreine*, m. p. 220° (decomp.); *m-acetyl-*

*aminobenzeneazohydrocupreine*, m. p. 155—180°; *m*-*carbamidobenzeneazohydrocupreine*, m. p. 165—185° (decomp.); *p*-*aminobenzeneazohydrocupreine*, m. p. 155—165°; *p*-*acetylaminobenzeneazohydrocupreine*, m. p. 158—162° (decomp.); *p*-*carbamidobenzeneazohydrocupreine*, decomposing at 190°; *p*-*hydroxybenzeneazohydrocupreine*, m. p. 150—160° (decomp.); *p*-*benzoyloxybenzeneazohydrocupreine dihydrochloride*, m. p. 185—195° (decomp.); *2*-*methoxybenzeneazohydrocupreine*, m. p. 120°; *3*-*methoxybenzeneazohydrocupreine*, m. p. 188—190°; *4*-*methoxybenzeneazohydrocupreine*, m. p. 213—215° (decomp.); *2*-*ethoxybenzeneazohydrocupreine*, m. p. 135—140°; *3*-*ethoxybenzeneazohydrocupreine*, m. p. 90—125°; *4*-*ethoxybenzeneazohydrocupreine*, m. p. 156—161°; *3*:*4*-*methylenedioxybenzeneazohydrocupreine*, m. p. 177—184°; *3*:*4*-*dimethoxybenzeneazohydrocupreine*, m. p. 110°; *3*-*methoxy-4*-*ethoxybenzeneazohydrocupreine*, m. p. 100—135°; *4*-*methoxy-5*-*ethoxybenzeneazohydrocupreine*, m. p. 75—120°; *3*:*4*-*dimethoxy-6*-*carboxybenzeneazohydrocupreine*, m. p. 236° (decomp.); *o*-*phenylglycollic acid*-*p*-*azohydrocupreine*,



m. p. 199—200° (decomp.); *m*-*carboxylamidobenzeneazohydrocupreine*, m. p. 195° (decomp.), gives a *dihydrochloride*; *p*-*sulphobenzeneazohydrocupreine*, m. p. 252° (decomp.) (compare Giemsa and Halberkann, *loc. cit.*); gives a scarlet *sodium salt*; *m*-*sulphonamidobenzeneazohydrocupreine*, m. p. 170—190°; *p*-*sulphonamidobenzeneazohydrocupreine*, m. p. 155—190°; *quinolyl-6*-*azohydrocupreine*, m. p. 232—234°; *benzeneazohydrocupreidine*, m. p. 183—185°, gives a *dihydrochloride*, m. p. 220—221° (decomp.); *α*-*naphthaleneazohydrocupreidine*, m. p. 132—140°; *p*-*nitrobenzeneazohydrocupreidine*, m. p. 135—139°; *p*-*sulphobenzeneazohydrocupreidine*, m. p. 247° (decomp.); *benzeneazo-6*-*hydroxyquinoline* has m. p. 160—161·5°. Most of these compounds show considerable softening or sintering and darkening previous to melting. W. G.

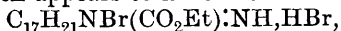
**Final Report on the Alkaloids of Gelsemium.** L. E. SAYRE (*J. Amer. Pharm. Assoc.*, 1919, **8**, 708—711).—The investigation was made on about 11·5 kilos. of the drug in N° 20 powder. The following alkaloids isolated as salts were obtained: *sempervirine nitrate* (about 3 grams), *gelsemine hydrochloride* (about 8 grams), *gelsemidine hydrochloride* (1·75 grams), and an amorphous alkaloidal chloride, which is named *gelsemoidine hydrochloride*. All of these are toxic.

CHEMICAL ABSTRACTS.

**Ethylmorphine Sulphate.** JAMES LESLIE THOMSON (*Pharm. J.*, 1920, [iv], **50**, 7).—Ethylmorphine sulphate has m. p. 207°, and crystallises with 5H<sub>2</sub>O; at 15·5° it dissolves in 9·5 parts of water and in 111 parts of 90% alcohol. W. P. S.

**Strychnine and Brucine.** VI. R. CIUSA (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 185—187).—The action of bromine on *isostrychnine* in acetic acid solution and subsequent decomposition of the *perbromide* yields derivatives of the *tribromo-base*,

$C_{21}H_{21}ON_2Br_3$ , in which two bromine atoms are added at a double linking as in strychnine, while the third replaces a hydroxyl group (A., 1915, i, 893). This conclusion is confirmed by the behaviour of *isostrychnine* towards (1) alcoholic hydrogen bromide in the hot, and (2) benzoyl chloride. The first of these reactions yields a crystalline compound which appears to have the formula



and is to be considered later.

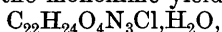
The action of benzoyl chloride on *isostrychnine* suspended in 10% potassium hydroxide solution yields only a small proportion of a compound, m. p.  $174^\circ$ . In pyridine solution, however, the benzoylation gives *benzoylisostrychnine*,  $C_{21}H_{21}O_2N_2Bz$ , which crystallises in colourless needles, m. p.  $174^\circ$ , and has the normal molecular weight in benzene solution. The benzoylation yields also the *benzoate* of the benzoyl derivative,  $C_{21}H_{21}O_2N_2Bz, BzOH, H_2O$ , which forms white needles, m. p.  $127^\circ$ . The *hydrochloride*,  $C_{21}H_{21}O_2N_2Bz, HCl$ , small, colourless needles, m. p.  $219^\circ$ ; the *aurichloride*, yellow needles, m. p.  $195^\circ$ ; and the *dichromate*,  $(C_{21}H_{21}O_2N_2Bz)_2, H_2Cr_2O_7$ , slender, reddish-yellow needles, were prepared and analysed. The sulphate and nitrate crystallise well, and are slightly soluble in water.

T. H. P.

**Strychnine Alkaloids. XXVII. Conversion of the Methyllummonium Salts from Brucine and apoMethylbrucine into Quinones.** HERMANN LEUCHS and WALTER HINTZE (*Ber.*, 1919, 52, [B], 2195—2204).—The salt of the quaternary ammonium base which is readily formed by the action of methyl sulphate on brucine shows, like the alkaloid itself, the red coloration with nitric acid, which is due to the formation of quinone; the latter, however, could not be isolated in the pure state or as a salt, and was therefore immediately reduced to the corresponding quinol, which separated from solution as a mixture of *bisapomethylbrucine methonitrate*,  $C_{21}H_{22}O_4N_2, MeNO_3, H_2O$ , colourless, shining prisms, and *acid sulphate*,  $C_{21}H_{24}O_5N_2, Me \cdot SO_4H$ , colourless, three-sided plates, in which the additional molecule of water appears to be chemically united, since it is not evolved in a vacuum at  $140^\circ$ . For purification the mixture of salts was transformed by 12*N*-hydrochloric acid into *bisapomethylbrucine methochloride*, leaflets or prisms (+  $1H_2O$ ), prisms (+  $2H_2O$ ),  $[\alpha]_D^{25} + 6.54^\circ$  for the monohydrated salt in aqueous solution. Oxidation of the quinol to quinone is conveniently effected with a solution of chromic acid in hydrochloric acid, whereby the *substance*,  $C_{21}H_{20}O_4N_2, MeCl, H_2CrO_4$ , bright red leaflets, is obtained, which is analogous to the compound derived from *bisapomethylbrucine* itself (A., 1911, i, 746). A similar oxidation is effected by heating the quinol with a solution of hydroxylamine in hydrochloric acid, when the *monoxime* of the quinone, yellow needles, is produced; this, however, has not the simplest formula,  $C_{22}H_{24}O_4N_3Cl$ , but contains an additional molecule of hydrogen chloride and, according to conditions, either  $4H_2O$ , which may be replaced in part by hydrogen chloride, or  $2H_2O$ . Concentrated nitric acid converts the chloride into the *nitrate*,



$C_{22}H_{24}O_4N_3(NO_3), HNO_3, 2H_2O$ , yellow prisms, which is hydrolysed by water to the *substance*,  $C_{22}H_{24}O_4N_3(NO_3), H_2O + H_2O$ , red prisms, which is re-converted by acid into the yellow nitrate. Similarly, the dichloride of the monoxime yields a hydrate,



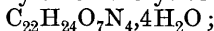
slender, red needles, when the excess of hydrochloric acid is removed preferably by addition of alkali hydroxide (1 mol.). By the aid of a second molecule of alkali hydroxide, the residual chlorine atom can be removed as hydrogen chloride, and a betaine-like *compound*,  $C_{22}H_{25}O_5N_3$ , orange-red prisms, is produced.

The yellow nitrate of the oxime is only formed with gently warmed nitric acid. At a higher temperature a more complex action occurs in which nitration is accompanied by oxidation of the quinone-oxime or nitrosophenol group to the nitrophenol group and a molecule of water is added; the nitrate,  $C_{22}H_{25}O_{11}N_5$ , which is thus produced, is identical with the product of the oxidation of the oxime of methylcacotheline (following abstract), from which it is more readily produced.

In a similar manner, *bisapomethylbrucine methochloride* is converted through the quinone by 5*N*-nitric acid at 50–60° into methylcacotheline methonitrate. On the other hand, only quinone formation, unaccompanied by nitration, is observed with concentrated nitric acid at 0°, so that in this instance, in contrast to that of *bisapomethylbrucine* itself (A., 1911, i, 746), it was not possible to obtain a nitrated but not hydrated quinone. H. W.

**Strychnine Alkaloids. XXVIII. Transformations and the Violet Colour Reaction of Methylcacotheline.** HERMANN LEUCHS and WALTER HINTZE (*Ber.*, 1919, 52, [B], 2204–2224. Compare A., 1919, i, 35).—Previous investigation of the methonitrate of the cacotheline bases (now termed methylcacotheline) had established the probability that it, in accordance with its mode of formation from brucine dimethosulphate, is a nitrated and hydrated quinone, but the function of the added water was left unexplained. Further evidence of its quinonoid nature is now adduced by the isolation of a *semicarbazone* as nitrate,  $C_{23}H_{27}O_7N_6 \cdot NO_3, 3H_2O$ , the *semicarbazone* of the methochloride, slender, pale yellow needles, and the *monophenylhydrazone* as nitrate,  $C_{28}H_{30}O_6N_5 \cdot NO_3, 3H_2O$ , brownish-red, oblique prisms. To determine whether water has been added in such a manner that the acid amide group  $\cdot CO-N^-$  of brucine has been converted into  $-CO_2H | H-N<$ , attempts have been made to identify the presence of the carboxyl group in two ways. On the one hand, hydrogen chloride has been removed from the semicarbazone hydrochloride by the agency of silver oxide (or, in general, a molecule of acid from the salts by a molecule of alkali), whereby a crystalline betaine,  $C_{23}H_{26}O_7N_6$ , has been produced which readily re-forms the original salts with acids. On the other hand, the presence of the carboxyl group is shown by the conversion of the semicarbazone nitrate into its *methyl ester*,  $C_{24}H_{29}O_7N_6Cl$ . The phenylhydrazone only yielded an amorphous betaine, but methylcacotheline itself gave a crystalline *betaine*,  $C_{22}H_{23}O_7N_3$ , and, as no

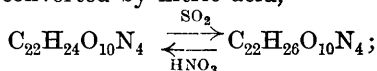
other acidic group can be present, may thus be regarded as containing the carboxyl group. The chloride of the monoxime described previously (*loc. cit.*) also yielded a crystalline *betaine*,



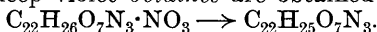
possibly, in this instance, the oxime or the tautomeric nitroso-phenol group could take part in the dehydration, but this view is rendered improbable by the isolation of a crystalline *monomethyl* and *monoethyl* ester.

The *nitrate* of the monoxime can only be obtained from the chloride by the use of metallic nitrates, since the oxime is oxidised when warmed with even *N*-nitric acid, the quinoneoxime or nitroso-phenol group being converted into the nitrophenol group, a second nitro-group being thus introduced into the molecule; this '*dinitrophenol*' also yields a crystalline *betaine*,  $\text{C}_{22}\text{H}_{24}\text{O}_8\text{N}_4$ , whilst its salts can be reduced to a '*diaminophenol*,'  $\text{C}_{22}\text{H}_{29}\text{O}_4\text{N}_4\text{Cl} \cdot 2\text{HCl}$  or  $1\text{HCl}$ , which can be obtained less smoothly from the nitroquinonemonoxime. According to these reactions, the formula of methylcatheline may be resolved thus:  $\text{C}_{16}\text{H}_{17}\{-\text{CO}-\text{CO}-; :\text{C}\cdot\text{NO}_2; \text{NMeNO}_3; =\text{NH}; \cdot\text{CO}_2\text{H}; =\text{CH}(\text{OH})\}$ .

The violet coloration caused by the action of stannous chloride or sulphur dioxide on methylcatheline has been previously investigated and attributed to the conversion of the quinone into the corresponding quinol, the necessary hydrogen being regarded as obtained by the conversion of the secondary alcoholic group of the brucine molecule into the keto-group. Further examination has now been made on the action of methylcatheline and similar salts towards sulphur dioxide in the presence of mineral acids; methylcatheline itself yields a crystalline, dark violet *nitrate*, which, however, contains two hydrogen atoms more than the original salt into which it is re-converted by nitric acid,



the corresponding chloride,  $\text{C}_{22}\text{H}_{24}\text{O}_7\text{N}_3\text{Cl}$ , similarly yields a violet *quinol*,  $\text{C}_{22}\text{H}_{26}\text{O}_7\text{N}_3\text{Cl}$ , from which it is re-formed by ferric chloride. The behaviour of the acid sulphate is precisely similar, the quinol sulphate re-forming the original material on treatment with ferric sulphate. The sulphite thus occupies a peculiar position in that reduction in this case only is caused by hydrogen derived from within the molecule. The presence of acid radicles which are not ionised is not essential to the production of the violet colour, since they can be removed by warming with one (or two) molecules of alkali, whereby deep violet *betaines* are obtained:



With the object of demonstrating the presence of the phenol group in the violet quinols, the violet chloride was boiled with acetic anhydride and sodium acetate; the *product*, however, did not contain the acetyl group, but was formed by loss of a molecule of hydrogen chloride and of water from the original substance. It appears to have a *betaine* structure, since it readily yields additive products with acids, and probably is a phenol *betaine*.

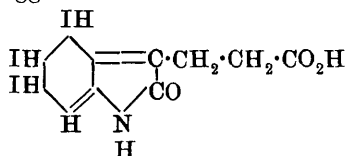
Reduction of the betaine anhydride,  $C_{22}H_{23}O_6N_3$ , with tin and hydrochloric acid yields the aminoquinol,  $C_{22}H_{26}O_4N_3Cl \cdot HCl \cdot 2H_2O$ , previously obtained from methylcactheline and formulated with  $1H_2O$ . A molecule of water appears to be eliminated during the reduction of methylcactheline in a manner similar to that observed during the action of acetic anhydride on the violet quinol. The composition of the amine hydrochloride varies considerably, and the following forms have been prepared and analysed:

$C_{22}H_{25}O_5N_3Cl \cdot HCl$ ,  
needles;  $C_{22}H_{25}O_5N_3Cl \cdot 2H_2O$ , trapezoidal tables;

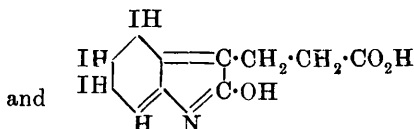
$C_{22}H_{26}O_5N_3Cl \cdot HCl$ ,  
rectangular or quadratc tables; from the first of these, hydrogen chloride is eliminated at  $100^\circ$ , whilst the third is stable at this temperature.

H. W.

**The Chemical Identification of Thyroxin. II.** E. C. KENDALL and A. E. OSTERBERG (*J. Biol. Chem.*, 1919, **40**, 265—334).—Thyroxin, the physiologically active constituent of the thyroid gland (A., 1919, i, 497), can exist in two tautomeric forms. The *keto*-form (I), which is by far the more stable, crystallises in long needles, m. p.  $250^\circ$ ; the enol form (II) crystallises in rosettes of needles, m. p.  $204^\circ$ . From a consideration of the chemical behaviour of the substance, so far as it is yet known, the authors suggest the formulæ



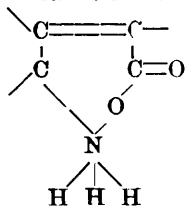
(I.)



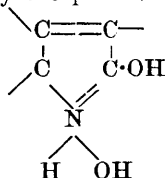
and

(II.)

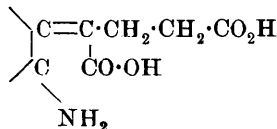
Further, there is evidence that by combination with the elements of a molecule of water, two further forms may exist, melting at  $225^\circ$  (III) and  $216^\circ$  (IV) respectively, the suggested nature of which is indicated by the partial formulæ



(III.)



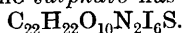
(IV.)



(V.)

Addition of an acid to the enolic form leads to fission of the ring and formation of an amino-acid (V), of which III is an internal salt. For the evidence on which the authors base these formulæ, the original must be consulted.

The *acetyl* derivative crystallises in short, curved needles, m. p.  $228-235^\circ$  (decomp.). The *sulphate* has the formula



The hydrochloride crystallises in star-shaped plates. When treated with cyanic acid, thyroxin yields a *carbamyyl* derivative,



Many mono- and di-basic metallic salts of thyroxin have been prepared, but although they are beautifully crystalline, they have not been obtained in a pure condition. A *dimethyl* ester has been prepared, and is hydrolysed to a *monomethyl* ester by alkali hydroxides.

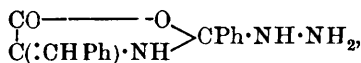
Thyroxin is not easily oxidised or reduced. When exposed to sunlight in weak alkaline solution, it is very unstable. Within twenty-four hours, the solution turns pink or yellow, deepening to a brown, and an aromatic odour is produced. The development of the pink colour is accompanied by the splitting off of iodine in the form of hypoiodous acid.

J. C. D.

**Constitution of Arylanthranils, Lactimides, and Lactimones.** GUSTAV HELLER and HILDE LAUTH (*Ber.*, 1919, 52, [B], 2295—2303).—In a previous communication (Heller, A., 1915, i, 844) it has been shown that acylanthranils react with hydrazine hydrate in alcoholic solution to yield 3-hydrazino-3-aryl-3:4-dihydrobenzoxazones, and the reaction is interpreted as in favour of the formula  $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CO} \\ \text{N} \cdot \text{COR} \end{array} \right\rangle$  for the acylanthranils, the behaviour being difficult to reconcile with the alternative formula  $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CO} \cdot \text{O} \\ \text{N} = \text{CR} \end{array} \right\rangle$ . A number of somewhat similarly constituted compounds have now been examined.

Anthranoylanthranilic anhydride and acetylanthranoylanthranilic anhydride (Schroeter, A., 1917, i, 529, 620) are converted by hydrazine hydrate in warm alcoholic solution into 3-hydrazino-3-o-aminophenyl-3:4-dihydrobenzoxazone, pale yellow needles, m. p. 200° (decomp.), and 3-hydrazino-3-o-acetylaminophenyl-3:4-dihydrobenzoxazone, colourless, thread-like crystals, m. p. 216° (decomp.); these substances are decomposed by alkali, and, on acidification with acetic acid, the lactone is re-formed in a somewhat impure condition. It appears, therefore, that complex acylanthranyls contain the same ring as is present in the simpler substances.

Benzoylaminocinnamic lactimide and acetylaminocinnamic lactimide react similarly with hydrazine hydrate, yielding, respectively, 5-keto-2-hydrazino-2-phenyl-4-benzylidenetetrahydro-oxazole,



colourless needles, m. p. 153—154° (*benzylidenehydrazino*-derivative, colourless needles, m. p. about 220° after darkening from 145°), and 5-keto-2-hydrazino-2-methyl-4-benzylidenetetrahydro-oxazole, coarse crystals and clusters of needles, m. p. about 180°

(decomp.) after darkening from 160°. For reasons similar to those advanced in the case of the acylanthraniols, the original substances must have the constitution  $\text{CHPh:C} \begin{smallmatrix} \text{CO} \\ \diagup \\ \text{N} \cdot \text{CO} \cdot \text{R} \end{smallmatrix}$ .

$\alpha$ -Benzoylaminoisobutyric anhydride (Mohr and Geis, A., 1908, i, 339; 1910, i, 117) is transformed by hydrazine hydrate into 5-keto-2-hydrazino-2-phenyl-4:4-dimethyltetrahydro-oxazole, slender needles, m. p. 134°, and must therefore have the lactam formula. The isomeric  $\alpha$ -benzoylaminoisobutyric hydrazide, obtained by the action of hydrazine hydrate on the acid chloride, has m. p. 248° (decomp.). H. W.

### Dyes Derived from Ketodihydro-1:4-benzisothiazine.

W. HERZOG (*Ber.*, 1919, 52, [B], 2270—2274).—Ketodihydrobenzothiazine reacts with  $\alpha$ -isatinanilide in a solvent of high boiling point, such as ethyl benzoate, to yield 2(2'-indoxyl)-3-ketodihydro-1:4-benzisothiazine (annexed formula), dull, brownish-violet needles with metallic glance, m. p. above 300°, which dyes cotton bluish-violet and wool reddish-violet. 2(2'-Thionaphthen)-3-ketodihydro-1:4-benzisothiazine, yellow, silky

needles, m. p. above 300°, prepared similarly from thionaphthenquinoneanilide, has little affinity for the textile fibres.  $\beta$ -Isatinanilide yields 2(3'-indoxyl)-3-ketodihydro-1:4-benzisothiazine, orange-red, silky needles, m. p. about 270°, which has very little affinity for the textile fibres.

The inferiority of the substances as dyes in comparison with indigo-blue and thioindigo-red is readily interpreted according to the Clauss hypothesis, since they contain only one quinonoid indogen, whilst the latter dyes contain two such groups. H. W.

**Certain Arylamino-derivatives of 4(5)-Methyl-5(4)-amino-methylglyoxaline and the Syntheses of 4(5)-( $\beta$ -p-Hydroxyphenylethyl- $\beta$ -aminoethyl)glyoxaline.** OTTO GERNGROSS (*Ber.*, 1919, 52, [B], 2304—2318).—The anil of 4(5)-methylglyoxaline-5(4)-aldehyde (Gerngross, A., 1912, i, 314) is reduced by sodium in boiling isoamyl-alcoholic solution in an atmosphere of hydrogen to

4(5)-methyl-5(4)-anilinomethylglyoxaline,  $\text{CH} \begin{smallmatrix} \text{NH} \cdot \text{CMe} \\ \diagdown \quad | \\ \text{N} - \text{C} \cdot \text{CH}_2 \cdot \text{NHPh} \end{smallmatrix}$ ,

slender needles from water, m. p. 183° (corr.) [*hydrochloride*, four-sided leaflets, m. p. 201° (corr.) after becoming discoloured at 175° and softening at 195°]; the corresponding benzoyl derivative crystallises in shining, four-sided plates, m. p. 206° (corr.), yields a *hydrochloride*, m. p. 235° (corr.), and does not couple with diazobenzenesulphonic acid in alkaline solution. The preparation of the aniline derivative is only conveniently effected in this manner when very small quantities of material are required; for larger

amounts, it is more conveniently produced by the action of aniline (2 mols.) on a solution of methylchloromethylglyoxaline hydrochloride (1 mol.) in methyl alcohol (compare Ewins, T., 1911, **99**, 2054); under these conditions, its formation is accompanied to a greater or less extent by that of *N*-phenyliminobis-4:5-dimethylglyoxaline,  $\text{NPh} \left( \text{CH}_2 \cdot \text{C} \begin{array}{l} \nearrow \text{CM} \cdot \text{NH} \\ \searrow \text{N} = \text{CH} \end{array} \right)_2$ , small needles, m. p. 199—200° (corr.), from which it can be readily separated by taking advantage of the very sparing solubility of the latter in boiling acetone.

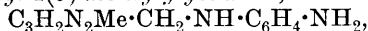
[With HANS NAST.]—The synthesis of 4(5)-(β-*p*-hydroxyphenylethyl-β-aminoethyl)glyoxaline,



is described, which is of pharmacological interest, since it contains the active principles of *Secale cornutum* and tyramine united to one another. 5(4)-β-Phenylethylaminomethyl-4(5)-methylglyoxaline is obtained by slowly adding a solution of the hydrochloride of 4(5)-methyl-5(4)-chloromethylglyoxaline in methyl alcohol to β-phenylethylamine dissolved in slightly methyl-alcoholic water; the crude product is converted successively into the *dipicrate*, prisms, m. p. 211° (corr.) after softening at 204°, and the *dihydrochloride*, shining, hygroscopic, crystalline leaflets, m. p. 254° (corr.; decomp.) [*aurichloride*, yellow crystals, m. p. 215° (corr.)]. Small quantities of β-phenylethyliminobis-4:5-dimethylglyoxaline,



are produced during this reaction, and this substance becomes the main product when care is not taken to maintain a constant excess of the amine; the *tripicrate*, shining, yellow crystals, m. p. 176° (corr.) after softening at 160°, the hygroscopic *hydrochloride*, and the *platinichloride*, which darkens above 200°, but does not melt below 270°, are described. Similarly, the hydrochloride of methylimidazolymethyl chloride and *p*-phenylenediamine yield 5(4)-*p*-aminoanilinomethyl-4(5)-methylglyoxaline,



the *trihydrochloride*, four-sided, rhombic plates, m. p. 257° (decomp.), and *dipicrate*, large, yellow crystals, m. p. 219—220° (decomp.), of which are described.

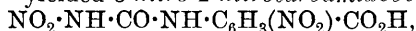
β-Aminoethylglyoxaline condenses with *p*-hydroxyphenylethyl chloride in methyl-alcoholic solution at 100° to yield 4(5)-(β-*p*-hydroxyphenylethyl-β-aminoethyl)glyoxaline; the crude product is treated with hydrochloric acid to remove the excess of the histamine base, and is purified by successive conversion into the *dipicrate*, m. p. 203·5° (corr.; decomp.), the *dihydrochloride*, colourless rods, m. p. 202—203° (corr.), and the free base, microscopic, four-sided prisms, m. p. 157° (corr.); the *monohydrochloride* forms four-sided platelets, m. p. 195° (corr.).

H. W.

**Quinazolines. XXXIV. The Synthesis of certain Nitro- and Amino-benzoyleneureas [Diketotetrahydroquinazolines] and some Compounds Related Thereto.** MARSTON

TAYLOR BOGERT and GEORGE SCATCHARD (*J. Amer. Chem. Soc.*, 1919, **41**, 2052—2068).—A supplement to, and an elaboration of, work previously published (compare A., 1916, i, 672), certain new compounds being described. Methyl anthranilate, when condensed with potassium isocyanate in acetic acid solution, yielded *methyl o-carbamidobenzoate*, m. p. 177—177·5° (corr.). 6-Nitro-2:4-diketo-1:2:3:4-tetrahydroquinazoline, m. p. 330—331° (corr.), gives a *sodium* salt, which is colourless at limit 7 on the Sørensen scale, but at 7·5 and on to 11 very slowly develops a greenish-yellow colour. The development of colour is, however, too slow for the salt to be of any use as an indicator. 6:8-Dinitrodiketotetrahydroquinazoline (*loc. cit.*) gives *potassium* and *ammonium* salts which resemble the sodium salt in general behaviour, except that the ammonium salt decomposes without explosion. The authors find higher m. p.'s for certain quinazoline derivatives than did Abt (compare A., 1889, 609). Thus 2:4-dichloroquinazoline has m. p. 119·5° (corr.); 2:4-dimethoxyquinazoline has m. p. 74°; 2:4-diketo-1:3-dimethyltetrahydroquinazoline has m. p. 167—168° (corr.).

*o*-Carbamidobenzoic acid when nitrated with nitric acid (D 1·5) at -5° to -10° yielded 5-nitro-2-nitrocarbamidobenzoic acid,



which it was very difficult to purify. Its *methyl* ester, decomposing at 184—185° (corr.), was obtained by nitration of methyl *o*-carbamidobenzoate. In an endeavour to clear up the chemistry of 5-nitro-2-acetylaminobenzoic acid, the authors have prepared a specimen, m. p. 218° (corr.), and its *barium*, *calcium*, *ferric*, *copper*, *lead*, and *silver* salts. Similarly, they prepared 5-nitro-2-amino-benzoic acid, m. p. 278° (corr.; decomp.), and its *sodium*, *potassium*, and *ammonium* salts. It gives a *methyl* ester, m. p. 168° (corr.).

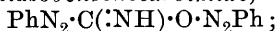
The proof that the compound obtained by Bogert and Geiger (compare A., 1912, i, 395, 510) by the nitration of 4-quinazolone is 6-nitro-4-quinazolone is supplied by the preparation of the same compound by fusing together 5-nitroanthranilic acid and formamide.

W. G.

**New Type of Substances Derived from Diazonium Compounds and Alkali Cyanides.** GUSTAV HELLER and MARIE MEYER

(*Ber.*, 1919, **52**, [B], 2287—2294).—When an aqueous solution of a benzenediazonium salt is added to a solution of potassium cyanide in the presence of an excess of potassium hydroxide, a yellow oil is formed, which immediately yields a colourless solution, from which an unstable, sparingly soluble, red salt gradually separates; this slowly decomposes, even in the cold liquid, with evolution of nitrogen and development of the odour of isocyanide. The corresponding free compound, however, is more stable and has the formula  $\text{C}_{13}\text{H}_{11}\text{ON}_5$ . The colour of the substance, its failure to yield hydroxylamine when treated with acids, and its reduction by

hydrogen to a colourless derivative lead the authors to consider it to be *benzenediazoxydiazobenzenecarbimide*,

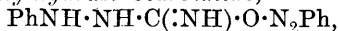


confirmatory evidence is deduced from the fact that it is only formed from *syn*-benzenediazonium hydrate and salt of hydrocyanic acid, and not from the *anti*-diazotate and substances which contain the cyano-group united to carbon or nitrogen.

The *potassium* salt of benzenediazoxydiazobenzenecarbimide forms dark red leaflets, m. p.  $239^\circ$  (decomp.), whilst the *sodium* salt consists of bronze-like leaflets, m. p.  $209^\circ$  (decomp.). The *lead*, *mercurous*, *manganese*, *silver*, *copper*, *cobalt*, *bismuth*, *stannous*, *cadmium*, *zinc*, and *mercuric* salts are described. The corresponding free substance crystallises in red needles, m. p.  $92^\circ$ , with violent evolution of gas. Attempts to obtain a benzoyl or methyl derivative were unsuccessful. *p*-Toluenediazoxydiazop-toluenecarbimide, m. p.  $111^\circ$  (decomp.), is converted by phenylcarbimide into *p*-toluenediazoxydiazop-toluenecarbimidophenylcarbamide,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_2\cdot\text{C}(\text{N}\cdot\text{CO}\cdot\text{NHPh})\cdot\text{O}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{Me}$ , orange-yellow crystals, m. p.  $148^\circ$  (decomp.). *o*-Toluenediazoxydiazoo-toluenecarbimide forms bluish-red rods, m. p.  $100^\circ$  (decomp.).

The sodium salt of benzenediazoxydiazobenzenecarbimide slowly decomposes in aqueous solution, yielding nitrogen, aniline, benzonitrile, ammonia, and nitrite, but not phenol. The free substance is decomposed by hot water, yielding smeary products, from which traces of phenol and benzonitrile could be isolated by distillation with steam.

The sodium salt of benzenediazoxydiazobenzenecarbimide is reduced by sodium hyposulphite in alkaline solution, by alkaline stannous chloride, by zinc dust, and acetic or hydrochloric acid in alcoholic solution, or by phenylhydrazine in alcoholic solution to *benzenediazoxyphenylhydrazinocarbimide*,



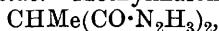
colourless needles or crystalline aggregates, m. p. about  $154^\circ$  (decomp.), which is converted by methyl sulphate into the corresponding *methyl* derivative, m. p.  $137$ – $138^\circ$  (decomp.). Protracted reduction of benzenediazoxydiazobenzenecarbimide by zinc and acid leads to the formation of aniline, whilst, in a similar manner, phenylhydrazine is formed when stannous chloride and hydrochloric acid act on a solution of the substance in glacial acetic acid. Benzenediazoxyphenylhydrazinocarbimide yields practically the same products as does the unreduced compound when it decomposes in cold alkaline solution; in acid solution, it is gradually decomposed, with the formation of phenol. *o*-Toluenediazoxy-*o*-tolylhydrazinocarbimide forms colourless crystals, m. p.  $150^\circ$  (decomp.).  
H. W.

**The Special Reactions in the Transformation of the Azides of Carboxylic Acids. I.—VI.** THEODOR CURTIUS (*J. pr. Chem.*, 1916, [ii], **94**, 273–382).—The “normal” reaction of the acid azides, and their formation, are summarised as follows:  $\text{R}\cdot\text{CO}_2\text{Et} \rightarrow \text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2 \rightarrow \text{R}\cdot\text{CO}\cdot\text{N}_3 \rightarrow \text{R}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$  or



$R \cdot NH \cdot CO \cdot NH \cdot R \rightarrow R \cdot NH_2$ , numerous examples of which have already been given in the case of mono-, di-, and even tri-carboxylic acids (most recent notices: A., 1914, i, 873; 1915, i, 124, 169, 787, 872). "Special" reactions are given by (1) the azides of acids having two  $-CO \cdot N_3$  groups attached to the same carbon atom, (2) by hydroxy-acids and their ethers, and (3) by  $\alpha$ -amino- and  $\alpha$ -acylamino-acids. In the first case, the ultimate products are generally the aldehydes or ketones produced by the hydrolysis of the methylenediamines,  $CHR(NH_2)_2$  or  $CRR'(NH_2)_2$ . Examples are now given. The second section is dealt with in Parts VII. to XIII. of this series (A., 1917, i, 635—639), and the third section in Parts XIV. to XVII. (A., 1918, i, 44).

I. [With WILHELM CÄSAR.]—*Hydrazide and Azide of Methyl- and isoAmyl-malonic Acids*.—Methylmalonodihydrazide,

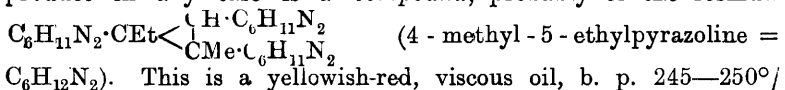


crystallises in silky needles, m. p.  $172-173^\circ$  (compare Bülow and Weidlich, A., 1906, i, 981), forms a *dihydrochloride*, m. p.  $168^\circ$ , a *dibenzylidene* compound, m. p.  $251^\circ$  (*ibid.*), a *disalicylidene* compound, glistening leaflets, m. p.  $216-217^\circ$ , a *diisopropylidene* compound, by boiling with acetone, minute needles, m. p.  $158-159^\circ$ , and a very explosive, yellow *diazide*,  $CHMe(CO \cdot N_3)_2$ . This reacts with aniline to form methylmalondianilide, m. p.  $182^\circ$  (Meyer and Bock, A., 1906, i, 726), and with *p*-toluidine to give the di-*p*-toluidide (Commanducci and Lobello, A., 1905, i, 271). It reacts with alcohol to form an oily urethane, which yields carbon dioxide and acetaldehyde on boiling with dilute sulphuric acid. *isoAmylmalonodihydrazide* forms silky crystals, m. p.  $140^\circ$  (decomp.), and gives a *dihydrochloride*, silky leaflets, a *dibenzylidene* compound, microscopic leaflets, m. p.  $240^\circ$ , and a *disalicylidene* compound, white tablets, m. p.  $186-187^\circ$ . The *diazide* is a pungent-smelling oil which reacts with aniline to give *isoamylmalondianilide*, silky needles, m. p.  $185^\circ$ , and with alcohol to form a urethane, this being hydrolysed by dilute sulphuric acid to *isohexaldehyde*,  $C_5H_{11} \cdot CHO$ . The aqueous distillate of the aldehyde reacts with benzhydrazide to give the *benzhydrazone*,  $C_5H_{11} \cdot CH : N \cdot NHBz$ , silky needles, m. p.  $215^\circ$ . *Dimethylmalonodihydrazide* crystallises in prisms, m. p.  $208^\circ$ , but gives poor results in the subsequent reactions, acetone being recognised, however, as the ultimate product. *Benzylmethylmalonodihydrazide* forms silky leaflets, m. p.  $260^\circ$ .

II. [With HEINRICH RECHNITZ.]—*Transformation of Ethylmalonazide into Propaldehyde, and Transformation of Propaldazine into 4-Methyl-5-ethylpyrazoline*.—Ethylmalonodihydrazide forms slender needles, m. p.  $168^\circ$  (compare Bülow and Bozenhardt, A., 1910, i, 233), and gives a *dihydrochloride*, m. p.  $180-181^\circ$ , a *dipicrate*, yellow needles, m. p.  $187^\circ$  (decomp.), a *dibenzylidene* compound, m. p.  $241-242^\circ$  (decomp.), and a *disalicylidene* compound, m. p.  $201^\circ$ . The *diazide* is very explosive, but may be converted into the dianilide and di-*p*-toluidide, m. p.  $288^\circ$ , or into the diurethane,  $CHEt(NH \cdot CO_2Et)_2$ , which is hydrolysed by dilute sulphuric acid to propaldehyde. The final yield is very poor,

however, as the yield of azide is only 35—40% to begin with. Propaldazine,  $N_2(\text{CHEt})_2$ , is a colourless oil with fishy odour, b. p. 143—145°,  $D_{20}^{19}$  0.844,  $n_D^{18}$  1.379, and it reacts with maleic acid in absolute alcohol to form *hydrazine maleate*,  $N_2H_4 \cdot C_4H_4O_4$ , very slender needles, m. p. 144° (decomp.), and 4-methyl-5-ethylpyrazoline,  $NH \left\langle \begin{array}{c} N \equiv CH \\ CHEt \cdot CHMe \end{array} \right.$ . This is a colourless liquid with the

odour of peppermint, b. p. 105—107°/18 mm., and is very stable in solution in dilute sulphuric acid. It gives blue and white precipitates with Fehling's solution and mercuric chloride respectively, but does not reduce these agents. With *p*-toluenediazonium sulphate it gives a brick-red compound, which dissolves in concentrated hydrochloric acid with deep bluish-violet colour, the solution becoming pale red on dilution. The yield of the pyrazoline is improved if the alcoholic mixture of propaldazine and maleic acid is heated, or if hydrazine maleate is mixed with propaldehyde, but the chief product in any case is a compound, probably of the formula

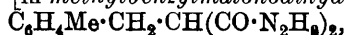


This is a yellowish-red, viscous oil, b. p. 245—250°/18 mm., which turns red litmus blue, but only forms oily salts. It has the reactions of the simple 4-methyl-5-ethylpyrazoline and is apparently formed by the elimination of two molecules of ammonia from four of the pyrazoline. The alkaline liquid left after the extraction of the two bases contains an amount of ammonia which agrees with this view, and fumaric acid is also present.

III. [With OWEN E. MOTT, repeated and in part amended by WILHELM SIEBER.]—*Hydrazide and Azide of Benzylmalonic Acid*.—*Benzylmalonodihydrazide*,  $CH_2Ph \cdot CH(CO \cdot N_2H_3)_2$ , crystallises in slender, glistening needles, m. p. 164°, forms a *dihydrochloride*, m. p. 135°, and a *dibenzylidene* compound, small needles, m. p. 220°, and changes into *secondary benzylmalonohydrazide*,  $CH_2Ph \cdot CH \left\langle \begin{array}{c} CO \cdot NH \\ CO \cdot NH \end{array} \right.$ , glistening leaflets, m. p. 241°, when

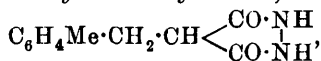
(a) its hydrochloride is kept in the moist condition or heated for some hours at 100°, (b) it is treated with alcoholic iodine, or (c) it is treated with sodium nitrite in the presence of a slight excess of hydrochloric acid. In the last reaction *benzylmalonyldiazide*, an explosive, yellow oil, is the chief product, and the by-product can be suppressed if an excess of acid is used. The diazide may be converted into the *dianilide*,  $CH_2Ph \cdot CH(CO \cdot NHPh)_2$ , m. p. 217°, and *diurethane*,  $CH_2Ph \cdot CH(NH \cdot CO_2Et)_2$ , a mass of very slender needles, m. p. 166°, the latter being hydrolysed by 2% sulphuric acid to phenylacetaldehyde, b. p. 81—82°/12 mm., which forms a *benzhydrazone*,  $CH_2Ph \cdot CH:N \cdot NHBz$ , needles, m. p. 148—149°, and a *m-nitrobenzhydrazone*, m. p. 152°.

IV. [With CARLO MARANGOLO.]—*Hydrazide and Azide of m-Xylylmalonic Acid* (*m-Methylbenzylmalonic Acid*).—*m-Xylylmalonodihydrazide* [*m-methylbenzylmalonodihydrazide*],



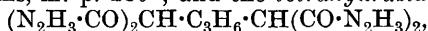
crystallises in silky needles, forms a hygroscopic *dihydrochloride*, m. p. 135—136° (decomp.), a *dibenzylidene* compound, small, glistening needles, m. p. 219°, a *disalicylidene* compound, m. p. 185—186°, a *diisopropylidene* compound, m. p. 182° (from acetone), and a *bisdiphenylmethylene* compound,

$$\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CPh}_2)_2,$$
 m. p. 164° (from benzophenone). The dihydrazide changes into the secondary *m-methylbenzylmalonohydrazide*,



m. p. 236—237°, when treated with alcoholic iodine. The unstable *diazide* may be converted into the dianilide, m. p. 193°, *di-p-toluidide*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_2$ , slender needles, m. p. 190°, and crude *diurethane*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}\cdot\text{CO}_2\text{Et})_2$ , which is hydrolysed by dilute sulphuric acid to *m-tolylacetaldehyde*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CHO}$ . This is a pleasant-smelling, pale yellow, refractive oil, b. p. 99—100°/18 mm., which forms an oily *phenylhydrazone*, a *benzhydrazone*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{N}\cdot\text{NHBz}$ , long needles, m. p. 129—130°, and a *m-nitrobenzhydrazone*, very pale yellow, prismatic needles, m. p. 115—116°.

V. [With GOTTFRIED GRANDEL.]—*Hydrazide and Azide of Pentane- $\alpha\alpha\epsilon\epsilon$ -tetracarboxylic Acid and of cycloButane-1:1-dicarboxylic Acid*.—The ethyl esters of these acids are obtained by adding a mixture of trimethylene bromide and ethyl malonate to a mass of sodium ethoxide in alcohol. If the mixture is added rapidly and the temperature is only controlled sufficiently to prevent undue violence, the yield of the pentane derivative rises to about 12%, but if the addition and cooling are carefully controlled, the yield of cyclic compound is improved. The latter is slightly volatile in steam, and may be slowly removed in this way from the non-volatile pentane compound. In any case, the yields are poor, and the reaction cannot be fully explained. Ethyl pentane- $\alpha\alpha\epsilon\epsilon$ -tetracarboxylate is a pleasant-smelling, viscous, colourless oil, b. p. 210—215°/12 mm., and ethyl cyclobutane-1:1-dicarboxylate is a limpid, highly refractive oil with the odour of camphor, b. p. 220—228° (compare Perkin, T., 1883—1891). The esters are converted into the amides and hydrazides by the action of ammonia or hydrazine in the usual way. *Pentane- $\alpha\alpha\epsilon\epsilon$ -tetracarboxylamide* forms soft prisms, m. p. 280°, and the *tetrahydrazide*,



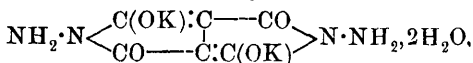
is a snowy powder, m. p. 200° (decomp.), which yields a *tetrahydrochloride*, m. p. 200°, a *platinochloride*,  $\text{C}_9\text{H}_{20}\text{O}_4\text{N}_8\cdot 2\text{H}_2\text{PtCl}_4$ , and a *tetrazylidene* compound, m. p. 248°. The *tetra-azide* is an odourless, white powder, which melts under benzene at 50—55°, is comparatively stable when dry, but explodes on rubbing. The *tetra-anilide* is obtained from the azide as a white powder, m. p. 285°. The azide also changes into an impure carbamide derivative when boiled with water, and into an oily urethane on boiling with alcohol, the latter giving a distillate containing glutardialdehyde,  $\text{C}_3\text{H}_6(\text{CHO})_2$ , when boiled with dilute sulphuric acid. *cycloButane-*

1:1-dicarboxylamide crystallises in long, rectangular prisms, m. p. 268°, and the dihydrazide,  $\text{CH}_2\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CH}_2\end{smallmatrix}\rangle\text{C}(\text{CO}\cdot\text{N}_2\text{H}_3)_2$ , forms stout tablets or short needles, m. p. 109—110°, and yields a dihydrochloride, m. p. 175—176° (decomp.), a platinumchloride,  $\text{B}_2\text{H}_2\text{PtCl}_4$ , a dipicrate, yellow needles, m. p. 185°, a dibenzylidene compound, m. p. 212—213°, a disalicylidene compound, m. p. 215°, and a diisopropylidene compound, m. p. 176—177°. For the conversion of the dihydrazide into the diazide, the temperature of the mixture must be kept well below  $-5^\circ$ , otherwise evolution of carbon dioxide and nitrogen takes place and a deep red solution is obtained.

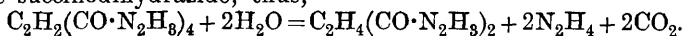
The diazide,  $\text{CH}_2\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CH}_2\end{smallmatrix}\rangle\text{C}(\text{CO}\cdot\text{N}_3)_2$ , is a colourless, lachrymatory oil, which can only be kept when moist for a short time as it is decomposed by water. cycloButane-1:1-dicarboxylanilide, m. p. 214—215°, and the di-p-toluidide, m. p. 247°, are obtained from the azide. The azide is hydrolysed to a considerable extent with the production of free hydrazoic acid when warmed with water or alcohol, but it also loses carbon dioxide and nitrogen, and when the product is acidified and distilled, cyclobutanone is found in the distillate. From the solution, cyclobutanonephenylhydrazone, a pure white, light mass of felted needles, or long needles from benzene, m. p. 95—96°, which can only be kept a few hours, and the stable semicarbazone, m. p. 211—212° (decomp.) (compare Demjanov and Dojarenko, A., 1908, i, 156), may be precipitated by adding the appropriate agents.

VI. [With HERMANN THIEMANN.]—Hydrazide and Azide of s.-Ethanetetracarboxylic Acid.—Ethanetetracarboxytetrahydrazide,  $\text{C}_2\text{H}_2(\text{CO}\cdot\text{N}_2\text{H}_3)_4$ , crystallises in slender needles, m. p. 205° (decomp.), and forms a tetrahydrochloride, m. p. 145—148° (decomp.), a tetrabenzylidene compound, m. p. 242°, a tetrasalicylidene compound, m. p. 213—214°, and a tetraisopropylidene compound,  $\text{C}_{18}\text{H}_{30}\text{O}_4\text{N}_3\cdot 4\text{H}_2\text{O}$ , m. p. 255°, which evolves dimethylketazine,  $\text{CMe}_2\cdot\text{N}\cdot\text{N}\cdot\text{CMe}_2$ , when heated at 110°. The conversion of the hydrazide into the tetra-azide (radiate groups of white crystals) only proceeds in the presence of an excess of hydrochloric acid which entails considerable loss of hydrazoic acid. The azide may be converted into the tetra-anilide, m. p. 240—242°, tetra-p-toluidide, m. p. 236—237°, and tetraurethane,  $\text{C}_2\text{H}_2(\text{NH}\cdot\text{CO}_2\text{Et})_4$ , white needles, m. p. 268°, the mother liquor from the latter preparation containing glyoxal. When the tetrahydrazide is warmed with water it changes into the yellow hydrazine salt of ethanetetracarboxytrihydrazide,  $\text{NH}_2\cdot\text{N}\langle\begin{smallmatrix}\text{CO} & \text{CH}\cdot\text{CO}\cdot\text{N}_2\text{H}_3 \\ \text{C}(\text{O}\cdot\text{N}_2\text{H}_3) & \text{C}\cdot\text{CO}\cdot\text{N}_2\text{H}_3\end{smallmatrix}\rangle$ , m. p. 142°, which reacts with acetone to form the triisopropylidene compound,  $\text{CMe}_2\cdot\text{N}\cdot\text{N}\langle\begin{smallmatrix}\text{CO}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}_2 \\ \text{CO}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}_2\end{smallmatrix}\rangle$  m. p. 138—140° (with  $3\text{H}_2\text{O}$ , m. p. 90—92°). This is converted into the tribenzylidene compound, m. p. 193—194°, by means of benzaldehyde, and then into the trihydrochloride, m. p. 182—183° (decomp.), by rubbing with

concentrated hydrochloric acid. The corresponding *triazide* is a very explosive, viscous oil, which may be converted into *ethane-tricarboxytrianilide*,  $\text{NHPh}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}\cdot\text{NHPh})_2$ , m. p. 223—224°, and *tri-p-toluidide*, m. p. 230°. The tetrahydrazide loses still more hydrazine residues when ground with bromine water or warmed with alcoholic iodine, the product being *ethanetetra-carboxy-dihydrazide*,  $\text{NH}_2\cdot\text{N}\langle\begin{smallmatrix}\text{CO}\cdot\text{CH}\cdot\text{CO} \\ \text{CO}\cdot\text{CH}\cdot\text{CO}\end{smallmatrix}\rangle\text{N}\cdot\text{NH}_2$ , which crystallises in highly refractive, glistening scales, m. p. 254—255°. This has both acidic and basic properties, forming a *dipotassium salt*,



pale yellow leaflets, m. p. 158°, a *dihydrazine salt*, m. p. 208°, a *diammonium salt*, m. p. 98°, which loses ammonia when kept, and a *hydrochloride*, m. p. 185—186° (decomp.). It also yields a *dibenzylidene* compound, m. p. 240—241°, a *disalicylidene* compound, m. p. 231—232°, a *diisopropylidene* compound, m. p. 261°, and a *tetra-acetyl* derivative, m. p. 202—203°. When treated with sodium nitrite and hydrochloric acid, the dihydrazide changes into *ethane-tetracarboxy-di-imide*,  $\text{NH}\langle\begin{smallmatrix}\text{CO}\cdot\text{CH}\cdot\text{CO} \\ \text{CO}\cdot\text{CH}\cdot\text{CO}\end{smallmatrix}\rangle\text{NH}$ , which crystallises in colourless leaflets, blackens at 265—270°, and forms a stable *disilver salt*,  $2\text{H}_2\text{O}$ . When boiled with water for a few hours, the tetra- or tri-hydrazides lose carbon dioxide as well as hydrazine and give succinodihydrazide, thus,



J. C. W.

**The Evolution of Proteins.** E. L. KENNAWAY (*Chem. News*, 1920, 120, 13—16).—After discussing the amino-acids which have been established as occurring commonly in proteins, the author draws attention to their very limited number, but great diversity, as regards structure. He then goes on to consider whether the simplest plants, for example, bacteria, yeasts, contain all these amino-acids present in the higher plants, and, taking the information available, shows that, with the exception of hydroxyproline, the presence or absence of which is not established, all the seventeen amino-acids considered are present in one or other of the five bacteria, yeast and mould, which have been examined. The two doubtful occurrences are serine and cystine. The author then discusses the bearing of these results on evolution, particularly on that of the higher animals, which are dependent on plant life for some of their essential amino-acids.

W. G.

**The Hydrolysis of Proteins in the Presence of Extraneous Materials and on the Origin and Nature of the "Humin" of a Protein Hydrosol.** R. A. GORTNER (*Science*, 1918, 48, 122—124; from *Physiol. Abstr.*, 1920, 4, 466).—A strong criticism of McHargue's statements regarding protein hydrolysis (compare A., 1918, ii, 280).

W. G.

**Action of Furfuraldehyde and Dextrose on Amino-acids and Protein Hydrolysates.** C. T. DOWELL and PAUL MENAUL (*J. Biol. Chem.*, 1919, **40**, 131—136).—It was observed that when whole plants, including the seed, are hydrolysed, a large amount of furfuraldehyde is given off, and that an unusually high percentage of humin nitrogen is obtained. No evidence of a reaction between glycine and furfuraldehyde was obtained, but there was an indication that reaction occurred with tyrosine and cystine. Only a slight amount of the humin nitrogen is due to adsorption. There is reaction between the hydrolysates of proteins and furfuraldehyde, which is particularly marked when the reaction takes place in neutral or acid solution. The greatest loss of amino-nitrogen occurs, however, when dextrose is present during hydrolysis, and it is therefore concluded that dextrose reacts directly with the amino-acids, and not through the intermediate formation of furfuraldehyde. Complete hydrolysis of proteins may be effected by heating in 10% hydrochloric acid for three hours at 20 lb. pressure.

J. C. D.

**Hydrolysis of Stizolobin, the Globulin of the Chinese Velvet Bean, *Stizolobium niveum*.** D. BREESE JONES and CARL O. JOHNS (*J. Biol. Chem.*, 1919, **40**, 435—448).—The globulin of the Chinese velvet bean has been hydrolysed and the percentages of the constituent amino-acids determined: 77·21% of the total protein was isolated as amino-acids and ammonia. Aspartic acid was determined both by the usual ester method and by Dakin's recently published process (Dakin, A., 1919, i, 150). The former method yielded 5·7% and the new process 9·23%. 2·81% of the recently discovered hydroxyglutamic acid was also obtained.

J. C. D.

**Solubility of Casein in Dilute Solutions of Sodium Chloride and its Dependence on the Hydrogen Ion Concentration.** SIGFRID RYD (*Arkiv. Kem. Min. Geol.* 1917, **7**, No. 1, 1—15).—The solubility of casein in dilute solutions of sodium chloride has been determined for thirty-two concentrations at 18—20°. The casein in weighed quantity was placed in a cylindrical vessel fitted with stirrer, thermometer, and two burettes. A quantity of a standard solution of sodium hydroxide, sufficient to dissolve the casein, but not an excess, was added, and the mixture stirred until solution had occurred. Then from one of the burettes standard hydrochloric acid was added until an opalescence was produced. The amount of sodium hydroxide taken in the first place was so chosen that the hydrochloric acid necessary to produce opalescence was slightly more than equivalent to the sodium hydroxide, the excess of acid was neutralised, and the casein redissolved by the addition of sodium hydroxide from the other burette. This process was continued until the acid and alkali, when exactly equivalent, just produced an opalescence. Hence the concentration of the solution on casein and sodium chloride was known. The solubility of casein in sodium chloride solution rises with increase in

the concentration of the sodium chloride to a maximum, which is reached with 0.1150*N*-sodium chloride. The following are the extreme values: 0.0365*N*-NaCl dissolves 0.64 mg. per c.c., 0.1150*N*-NaCl dissolves 3.46 mg. per c.c., and 0.2725*N*-NaCl dissolves 1.32 mg. per c.c. The hydrogen-ion concentration of each saturated solution was determined at 21°, and it is found that this quantity is practically constant at  $5.13 \times 10^{-6}N$ , from which it follows that opalescence in solutions of casein occurs when the hydrogen-ion concentration has the above value and this lies very near the iso-electric point, which has a value  $1.1 \times 10^{-4}$ — $7.9 \times 10^{-6}$ .

J. F. S.

### Hæmocyanin. I. Recrystallisation of Oxyhæmocyanin.

AUREL D. CRAIFALEANU (*Boll. Soc. Nat. Napoli.*, 1918, **31**, 88—99).—The author describes the crystallisation of hæmocyanins from the blood of *Octopus vulgaris*, *O. macropus*, and *Eledone moschata*, following the methods described by Hofmeister and by Hopkins and Pinkus for the crystallisation of egg-albumin.

The hæmocyanin derived from the blood of *O. vulgaris* may crystallise in three different forms: short needles, rosettes of needles, and relatively large crystals, which, from their appearance under the microscope, the author terms "projectile" crystals. These forms vary with the conditions of crystallisation. The hæmocyanin from *O. macropus* was obtained in long, needle-shaped crystals. On allowing the glass containing the crystals and mother liquor to remain for some time, the crystals become insoluble, and this modification is termed *parahaemocyanin*. The pigment from the blood of *E. moschata* crystallises in needles. The so-called "projectile" crystals are characteristic of the hæmocyanin from *O. vulgaris*.

J. C. D.

### Crystalline Salts of Uridinephosphoric Acid. P. A.

LEVENE (*J. Biol. Chem.*, 1919, **40**, 395—398. Compare A., 1918, i, 130).—The normal ammonium salt is readily prepared from the brucine salt, and crystallises in heavy, elongated prisms, decomp. 185° (uncorr.). In aqueous solution it has  $[\alpha]_D^{20} + 21.0^\circ$ , and crystallises with 1H<sub>2</sub>O. The ammonium hydrogen salt crystallises in long, prismatic needles,  $[\alpha]_D^{20} + 13.0^\circ$ , contracts at 210° (corr.), decomp. at 242° (corr.). Normal lead salt, long needles. Brucine salt, C<sub>9</sub>H<sub>13</sub>O<sub>9</sub>N<sub>2</sub>P(C<sub>23</sub>H<sub>26</sub>O<sub>4</sub>N<sub>2</sub>)<sub>2</sub>·7H<sub>2</sub>O,  $[\alpha]_D^{20} - 20.0^\circ$  (in very dilute solution). Air-dried substance effervesced at 185° (corr.), and contracted and melted without further decomposition at 195° (corr.).

J. C. D.

### Crystalline Guanylic Acid. P. A. LEVENE (*J. Biol. Chem.*,

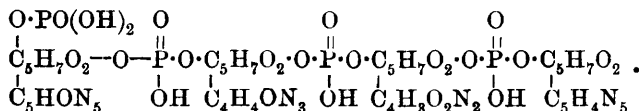
1919, **40**, 171—174).—The crude brucine salt of guanylic acid was converted into the ammonium salt and precipitated from aqueous solution with neutral lead acetate. The solution obtained after removal of lead from the precipitate yielded, on concentration under diminished pressure, a crystalline substance. Analysis corresponded

with the formula  $C_{10}H_{14}O_8N_5 \cdot \frac{1}{2}H_2O$ ,  $[\alpha]_D^{20}$  in aqueous solution  $-7.5^\circ$ . In 5% aqueous ammonia,  $[\alpha]_D^{20} -43.5^\circ$ . In 10% hydrochloric acid it was optically inactive. The substance had all the properties of guanylic acid. It gelatinised in the presence of mineral impurities and turned brown at  $208^\circ$ . The brucine salt,  $C_{56}H_{64}O_{16}N_9 \cdot 7H_2O$ , contracted at  $217^\circ$ , melted at  $233^\circ$ , and effervesced at  $240^\circ$ ;  $[\alpha]_D^{20} -26.0^\circ$  in 35% alcohol. J. C. D.

**The Structure of Yeast-Nucleic Acid. IV. Ammonia Hydrolysis.** P. A. LEVENE (*J. Biol. Chem.*, 1919, **40**, 415—424).—The original graphic representation of the entire molecule of yeast-nucleic acid had only an arbitrary schematic sense (compare Levene and Jacobs, A., 1909, i, 620, 686; 1911, i, 96, 510). The views as to structural formulæ advanced by Jones (A., 1917, 232, 233, 596, 597) and by Thannhauser (A., 1914, i, 1015; Thannhauser and Dorfmueller, A., 1918, i, 47) and the evidence adduced in their support are considered.

Nucleic acid was hydrolysed in a 2.5% aqueous ammonia solution for one hour at  $100^\circ$ , a milder treatment than that employed by either Jones or Thannhauser. It is proved that the adenine-uridine dinucleotide is a mixture of two mononucleotides. The fraction originally regarded by Jones as a guanine-cytosine dinucleotide was found to consist principally of guanosinephosphoric acid, together with a small proportion of uridinephosphoric acid. The present findings nullify the experimental evidence in support of the theories of Jones and Thannhauser. From the theoretical point of view, the theory of Thannhauser is weak because it assumes a carbon to carbon linking, which is a very strong type of union, whereas the polynucleotide is readily dismembered into mononucleotides. The ether linking accepted by Jones is also a very firm union.

On the basis of considerations such as these the linking of the nucleotides could be expressed most simply in the following way:



For the present this formula expresses the facts known about the structure of yeast-nucleic acid. Whether it will require alteration or not, it is certain that the polynucleotide structure of yeast-nucleic acid is definitely established. J. C. D.

**The Combination of Enzyme and Substrate. I. Estimation of Pepsin. II. The Effect of the Hydrogen Ion Concentration.** JOHN H. NORTHROP (*J. Gen. Physiol.*, 1919, **2**, 113—122).—The change in the conductivity during the digestion of egg-albumin by pepsin affords a convenient and accurate method for the estimation of pepsin. The changes in conductivity do not follow the actual rate of digestion, but the percentage change in conductivity is constant for a given quantity of pepsin, irrespective of the absolute value of the original conductivity. It was found



that the maximum change occurred in strong solutions of egg-albumin titrated to  $p_H$  2.6 with hydrochloric acid. By this process it is possible to determine quantitatively the amount of pepsin removed from solution by various substances.

A series of experiments with substances such as starch, calcium sulphate, agar, kaolin, blood-charcoal, caseinogen, and egg-albumin gave results which indicate that the removal of pepsin from solution is not purely a matter of surface, but that it is dependent in some way on the substance itself. That is, the equilibrium reached is independent of the size of the particles, and therefore of their surface. This would indicate that the process is either one of solution, in which case the law of partition-coefficients should be found to hold, or of chemical combination, in which case the law of mass action should apply.

Preliminary experiments indicate that the process follows the law of partition-coefficients.

There is a decided optimum hydrogen-ion concentration for the combination of pepsin with its substrate corresponding with the optimum reaction for digestion. It is suggested that the combination of pepsin with its substrate, and hence the rate of digestion, is governed by the quantity of ionised protein present. J. C. D.

**The Different Actions of Pepsin and Chymosin on Acid Solutions of Syntonin.** OLOF HAMMARSTEN (*Medd. K. Vetenskaps-akad. Nobel-Inst.*, 1919, 5, No. 7, 1—13).—In previous papers (compare A., 1918, i, 459, 510) the author has put forward evidence in support of assigning separate identities to chymosin and pepsin. Further support to his views is given by the experiments detailed in the present paper, syntonin obtained from fish or horseflesh being used in place of acid and alkali legumin (A., 1918, i, 510). The method of experiment was similar to that previously detailed, and all the results indicate that chymosin acts on syntonin, forming albumoses, at an acid concentration at which pepsin is inactive.

T. S. P.

**Catalase.** EIICHI YAMAZAKI (*J. Tokyo Chem. Soc.*, 1919, 40, 514—522).—The author has previously deduced an equation (*ibid.*, 35 and 36) by which it is possible to describe the course of the reaction between catalase and hydrogen peroxide at any temperature and any initial concentrations by using the temperature-coefficient and the value of  $k$  at 18°. He now finds that, contrary to Evans's statement (A., 1907, i, 456), even with a range of concentration from 1 to 80,  $k/E_0$  is constant provided the hydrogen-ion concentration is kept constant. Blood catalase, prepared by the method of Senter (A., 1903, ii, 661), is diluted to less than 1%, 20 c.c. of 0.02*N*-sodium hydrogen carbonate are added to each solution of the enzyme, the volume is made up to 130 c.c. at 25°, and 20 c.c. of 0.028*N*-hydrogen peroxide are added. The estimations are made in a current of carbon dioxide.

The author discusses the kinetics of catalase action, and is of opinion that the action is purely chemical.

CHEMICAL ABSTRACTS.

**Urease and the Radiation Theory of Enzyme Action. IV.**

H. P. BARENDRECHT (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 126—138. Compare A., 1919, i, 604; this vol., i, 102).—A continuation and completion of previous work. The accelerating action observed with urease and attributed by previous experimenters to carbon dioxide is shown to be non-existent. Ammonium carbonate and carbon dioxide form a powerful buffer mixture which can maintain a constant  $P_H$  value, the essential condition for constant enzyme activity in a urea solution during hydrolysis by urease. The estimation of initial velocities of hydrolysis, equal concentrations of urease being allowed to act on different concentrations of urea at constant  $P_H$  and  $T$  values, produces results which appear inexplicable without the radiation theory. The lower the value of  $P_H$  the more the initial velocities increase with increase in the urea concentration. With high  $P_H$  values there is first an increase and then a decrease on raising the urea concentration. These facts are strictly in accordance with the radiation hypothesis. The urease radiation, weakened by spreading or in any other way, may effect synthesis. This is indicated by the fact that at high  $P_H$  values, where the urease is shown to be decaying, reversion of an hydrolysis has been observed. From the last fact it is deduced that outside the sphere of hydrolytic action around a urease molecule there must be a region of radiation, weakened by spreading, and therefore of synthesis. This is confirmed by the fact that on diluting the urease concentration beyond a certain value, its specific activity is decreased. From this it is evident that the synthetic action of urease, which is not decaying, can only come into play when the spheres of hydrolytic action do not intersect one another. It is shown experimentally that in any urease solution in which the enzyme is decaying through the combined action of alkalinity, temperature, and time, a synthesis of urea from ammonium carbonate, proportional to the urease concentration, is observed. A description of an apparatus for determining the concentration of hydrogen and hydroxyl ions is included in the paper. J. F. S.

**Cyanodiphenylarsine.** GIUSEPPE STURNIOLO and GIACOMO BELLINZONI (*Boll. Chim. Farm.*, 1919, **58**, 409—410\*).—*Cyanodiphenylarsine*,  $\text{AsPh}_2\cdot\text{CN}$ , crystallises in almost colourless, apparently monoclinic plates, m. p.  $35^\circ$ , having the odour of both garlic and bitter almonds, hydrogen cyanide being liberated readily by the action of moist air; its odour irritates the nasal mucus, provoking sneezing. By treatment with aqueous or alcoholic alkali hydroxide, or by heating with water, or by distillation either in a current of steam or under reduced pressure (100 mm.), it is converted into diphenylarsine oxide,  $(\text{AsPh}_2)_2\text{O}$ . When treated either with concentrated nitric acid on the water-bath or with 2% hydrogen peroxide, or with bromine water in the cold, it yields diphenylarsinic acid. Both cyanodiphenylarsine and diphenylarsine oxide, containing trivalent arsenic, are transformed into diphenylarsinic acid, in

\* and *Gazzetta*, 1919, **49**, ii, 326—327.

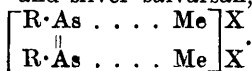
which the arsenic is quinquivalent, by the traces of hydrogen peroxide sometimes occurring as impurities in ether and in light petroleum. The alkali salts of diphenylarsinic acid are soluble, whereas the iron salt forms a very fine, white, insoluble powder and decomposes when heated.

T. H. P.

**Tetraphenyldiarsine.** C. W. PORTER and PARRY BORGSTROM (*J. Amer. Chem. Soc.*, 1919, **41**, 2048—2051).—The authors have prepared tetraphenyldiarsine in a pure state from the oxide by the method of Michaelis and Schulte (compare A., 1883, 187), and distributed it into sealed glass tubes without allowing it to come into contact with air. So prepared, when exposed to air it oxidises to diphenylarsinic acid and tetraphenyldiarsine oxide, but is not spontaneously inflammable, as reported by Michaelis (compare A., 1902, i, 515). In benzene solution it gradually absorbs oxygen. In similar solution it rapidly absorbs iodine, giving a crystalline iodo-compound, m. p.  $30^{\circ}$ , which is probably diphenyliodoarsine. Its vapour pressure at  $200^{\circ}$  is about 1 mm., and at  $300^{\circ}$  in a vacuum it decomposes, giving arsenic and triphenylarsine, and consequently its molecular weight in the state of vapour cannot be determined. Molecular weight determinations by the cryoscopic method in naphthalene indicate that tetraphenyldiarsine is associated at the freezing point of naphthalene.

W. G.

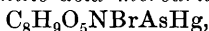
**The Constitution of Arseno-metallic Compounds.** P. KARRER (*Ber.*, 1919, **52**, [B], 2319—2324).—In reply to Kolle (*Deut. med. Woch.*, 1918, 1177) and Binz, Bauer and Hallstein (*Arbb. aus Inst. exp. Therapie Georg Speyer Haus*, 1919, **25**, 45), the author maintains the correctness of the views advanced by Ehrlich and Karrer (A., 1916, i, 95), that the metal in complex salts, such as copper- and silver-salvarsan, is directly united to the arsenic atom, thus,



H. W.

**Chemotherapeutic Studies on Organic Compounds containing Mercury and Arsenic.** GEORGE W. RAIZISS, JOHN A. KOLMER, and JOSEPH L. GAVRON (*J. Biol. Chem.*, 1919, **40**, 533—552).—The following are described: 3-Nitroarsanilic acid mercuriacetate,  $\text{OAc} \cdot \text{Hg} \cdot \text{C}_6\text{H}_2(\text{NO}_2)(\text{NH}_2) \cdot \text{AsO}(\text{OH})_2$ , bright yellow powder soluble in dilute sodium hydroxide on warming. 3-Nitro-4-hydroxyphenylarsinic acid mercuriacetate,  $\text{C}_8\text{H}_8\text{O}_8\text{NAsHg}$ , yellow powder soluble in dilute sodium hydroxide. 3:5-Dinitro-4-hydroxyphenylarsinic acid mercuriacetate,  $\text{C}_8\text{H}_7\text{O}_{10}\text{N}_2\text{AsHg}$ , bright yellow powder partly soluble in dilute sodium hydroxide. 3-Amino-4-hydroxyphenylarsinic acid mercuriacetate,  $\text{C}_8\text{H}_{10}\text{O}_6\text{NAsHg}$ , brown powder soluble in dilute sodium hydroxide; the solution decomposes on keeping, with deposition of metallic mercury. 3:5-Diamino-4-hydroxyphenylarsinic acid mercuriacetate,  $\text{C}_8\text{H}_{11}\text{O}_6\text{N}_2\text{AsHg}$ , dark brown powder soluble in very dilute sodium hydroxide; the solution

decomposes, with formation of metallic mercury. *4-Carboxyphenyl-arsinic acid mercuriacetate*,  $C_9H_9O_7AsHg$ , cream-coloured powder insoluble in dilute sodium hydroxide, soluble in dilute hydrochloric acid, concentrated sodium chloride solution, and in glacial acetic acid on warming. *Diacetyl-3:5-diamino-4-hydroxyphenylarsinic acid mercuriacetate*,  $C_{12}H_{15}O_8N_2AsHg$ , grey powder soluble in dilute sodium hydroxide to form a brown solution, from which mercury is deposited. *3-Bromoarsanilic acid mercuriacetate*,



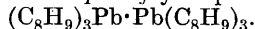
white powder soluble in dilute sodium hydroxide, warm glacial acetic acid, and 10% hydrochloric acid. *3-Bromo-oxalylarsanilic acid mercuriacetate*,  $C_{10}H_9O_8NBrAsHg$ , white powder soluble in dilute sodium hydroxide; the solution deposits metallic mercury on keeping.

All the above compounds are insoluble in the usual organic solvents. The presence of the arsenic acid group in the molecule of organic compounds apparently does not interfere with the entrance of the mercury group. As a class, this type of compound is comparatively stable in alkaline solution, the splitting off of mercury occurring only in compounds containing an amino-group. The toxic effect on the animal body appears to be caused mainly by the mercury group. These new compounds were not found to be superior to the ordinary organic mercury compounds as regards curative influence in experimental trypanosomiasis and germicidal effect in vitro.

J. C. D.

**Lead Triaryl, a Parallel to Triphenylmethyl.** ERICH KRAUSE and MARIA SCHMITZ (*Ber.*, 1919, **52**, [B], 2165—2170).—Indications of the formation of unsaturated organo-derivatives of lead, in which the metal is attached to carbon atoms by fewer than four valencies, have been previously observed, but the isolation of such substances has hitherto been impossible. The authors have succeeded in preparing lead tri-*p*-2-xylyl in the crystalline condition, and have shown that unsaturated derivatives are also formed to a greater or less extent by the action of magnesium phenyl or *p*-tolyl bromide on lead dichloride.

*Lead tri-p-2-xylyl*,  $Pb(C_6H_3Me_2)_3$ , is prepared by the addition of finely powdered lead dichloride to an ethereal solution of the calculated quantity of magnesium *p*-2-xylyl bromide; the bulk of the dichloride dissolves to a brownish-yellow or chestnut-brown solution of the diaryl compound, which gradually at the ordinary temperature, but more rapidly when heated, deposits lead and yields the lead triaryl. The substance forms a pale yellowish-green, heavy, crystalline powder which, under the microscope, appears to be formed of colourless, well-developed rhombs. Determinations of the molecular weight by the cryoscopic method in benzene solution indicate the formula  $[(C_6H_3)_3Pb]_2$ , so that the compound may possibly be regarded as hexa-*p*-2-xylyl diplumban,



The colour of the substance, however, points to a feeble union of

the lead atoms and to the possibility of dissociation under the influence of light. Probably the lead atoms are united in much the same manner as the methane carbon atoms of the triaryl-methyls. As is to be expected, the substance is readily attacked by chemical reagents; thus, when treated with bromine in pyridine solution at  $-40^{\circ}$ , it gives *lead tri-p-2-xylyl bromide*, four-sided leaflets, m. p.  $177^{\circ}$ , whilst in chloroform solution at  $-10^{\circ}$  it yields *lead di-p-2-xylyl dibromide*, colourless, shining rods, m. p.  $120^{\circ}$ . Lead tri-*p-2-xylyl* is remarkably stable towards air, and is not oxidised either in the solid state or in solution, although in the latter condition it is rapidly and completely decomposed on exposure to light. It is not sensitive to rise of temperature, and decomposition does not occur until  $220^{\circ}$ ; for this reason, attempts to obtain *lead tetra-p-2-xylyl* by the action of magnesium *p-2-xylyl* bromide on lead chloride at elevated temperatures were unsuccessful, but the compound was readily prepared from lead tri-*p-2-xylyl* bromide and the Grignard reagent; it forms colourless, rectangular plates, m. p.  $255^{\circ}$ , which decompose above  $270^{\circ}$ , with separation of lead.

H. W.

**Mixed Lead and Tin Aryls and Aryl Alkyls and their Application to the Synthesis of Organo-compounds of Silver. Examples of the Influence of Symmetry on the Properties of Chemical Compounds.** ERICH KRAUSE and MARIA SCHMITZ (*Ber.*, 1919, **52**, [B], 2150—2164).—The conversion of the readily accessible lead aryl monohaloids and tin aryl monohaloids (A., 1918, i, 415) into mixed aryl and aryl alkyl compounds is described. Asymmetry in the latter appears to impart to the compounds lower m. p. and greater solubility and chemical activity, which is explained by the assumption that the metallic atom is more completely protected from contact with a reagent by the symmetrical union with, for example, four phenyl groups, whilst with unlike groups spaces are left, through which the reagent can penetrate. The lead and tin aryls or aryl alkyls react with a cold alcoholic solution of silver nitrate, yielding bright yellow precipitates, which could not always be isolated in a pure condition, but which are shown in the cases of lead and tin triphenylethyls to have the composition  $2\text{PhAg}, \text{AgNO}_3$ .

*Mixed Lead Aryls and Aryl Alkyls.*—The compounds are prepared by the addition of lead triphenyl bromide to an ethereal solution of the magnesium aryl bromide, and are isolated in the usual manner. Unnecessarily protracted heating and long exposure of the crude products or their solutions to light and the air of the laboratory are to be avoided. The yields are almost quantitative. The following substances are described: *lead triphenyl p-tolyl*, hair-like needles, m. p.  $125.5^{\circ}$ ; *lead triphenyl p-2-xylyl*, transparent crystals, m. p.  $104.5^{\circ}$ ; *lead triphenyl m-4-xylyl*, rods arranged in clusters, m. p.  $111.5-112^{\circ}$ ; *lead triphenyl p-phenetyl*, small, shining needles, m. p.  $119-120^{\circ}$ ; *lead triphenyl  $\alpha$ -naphthyl*, colourless needles grouped in rosettes, m. p.  $101^{\circ}$ ; *lead triphenyl cyclo-*

*hexyl*, m. p.  $119^{\circ}$ ; *lead triphenyl ethyl*, needles, m. p.  $42^{\circ}$ ,  $n_{\text{H}_a}^{61}$  1.62628,  $D_4^{61}$  (vac.) 1.5885; *lead diphenyl di- $\alpha$ -naphthyl* (from lead diphenyl dibromide and magnesium  $\alpha$ -naphthyl bromide), microscopic prisms, m. p.  $197^{\circ}$ ; *lead di- $\alpha$ -naphthyl diethyl*, intergrown prisms, m. p.  $116^{\circ}$ .

*Mixed Tin Aryls and Aryl Alkyls*.—These are prepared from tin triphenyl chloride and excess of magnesium aryl or alkyl haloid in almost quantitative yield. The following substances are described: *tin triphenyl p-tolyl*, small, slender needles, m. p.  $124^{\circ}$ ; *tin triphenyl p-2-xylyl*, coarse, six-sided plates, m. p.  $100.5^{\circ}$ ; *tin triphenyl  $\alpha$ -naphthyl*, colourless prisms, m. p.  $125^{\circ}$ ; *tin triphenyl methyl*, large, shining rhombs, m. p.  $60^{\circ}$ ,  $D_4^{63.85}$  (vac.) 1.3113,  $n_{\text{H}_a}^{63.85}$  1.6001,  $n_{\text{D}}^{63.85}$  1.60661,  $n_{\text{H}_\beta}^{63.85}$  1.62351,  $n_{\text{H}_\gamma}^{63.85}$  1.63831; *tin triphenyl ethyl*, ice-like crystals, m. p.  $56^{\circ}$ ,  $D_4^{62}$  (vac.) 1.2953,  $n_{\text{H}_a}^{62}$  1.59917,  $n_{\text{D}}^{62}$  1.60542,  $n_{\text{H}_\beta}^{62}$  1.62236; *tin tetra-o-tolyl* (by action of a large excess of magnesium o-tolyl bromide on a suspension of the etherate of stannic chloride), white, crystalline powder, m. p.  $158$ — $159^{\circ}$ .

*Action of Mixed Lead and Tin Aryls on Silver Nitrate and Mercuric Chloride*.—*Silver phenyl silver nitrate*,  $2\text{PhAg}, \text{AgNO}_3$ , is prepared by the cautious addition of a solution of lead triphenyl ethyl in absolute alcohol to an alcoholic solution of silver nitrate. It forms a canary-yellow, amorphous powder resembling cadmium sulphide in shade. The colour deepens rapidly when the substance is heated until decomposition occurs at about  $100^{\circ}$ , the exact temperature depending both on the rate of heating and on the age of the preparation. It explodes when heated in a test-tube. The colour is practically unchanged after twelve hours in complete darkness, but darkens within a few minutes on exposure to diffused light. Similarly, lead triphenyl ethyl and mercuric chloride yield mercury phenyl chloride, leaflets, m. p.  $250^{\circ}$ . Tin triphenyl ethyl gives silver phenyl silver nitrate and mercury phenyl chloride with silver nitrate and mercuric chloride respectively, the products being identical with those prepared from the lead compound. Lead triphenyl *p*-phenetyl and silver nitrate yield a *product* which closely resembles the silver compound described above, but does not appear to be homogeneous. Lead tetraphenyl, tetra-*p*-tolyl, and tetra-*p*-2-xylyl are not acted on by cold alcoholic silver nitrate solution, but the solid compounds become grey, owing to the gradual reduction of the silver nitrate on protracted boiling of the solution. Lead triphenyl *p*-tolyl, triphenyl *p*-2-xylyl, and triphenyl *m*-4-xylyl have no action in dilute solution, or only cause a yellow coloration; with excess of concentrated silver nitrate solution, immediate precipitates closely resembling silver phenyl silver nitrate are formed, which give a colourless solution in the boiling solvent, and then yield a silver mirror and a brownish-yellow precipitate. Lead triphenyl  $\alpha$ -naphthyl, diethyl dinaphthyl, and triphenyl cyclohexyl yield immediate precipitates, even in dilute solution, which are very similar to one another in appearance and reactions, except in colour of the naphthyl compounds, which is orange-yellow; the latter substances yield naphthalene when treated with hydrochloric acid.

Lead diphenyl di-*a*-naphthyl does not react with alcoholic silver nitrate.

The aromatic tin compounds react less readily than the corresponding lead compounds. Tin tetraphenyl does not react; tin triphenyl *p*-tolyl and triphenyl *p*-2-xylyl do not act in cold solution, and cause reduction when boiled. Tin triphenyl phenetyl gives a yellow precipitate after a few seconds, whilst tin triphenyl methyl, like the ethyl compound, gives an immediate precipitate of silver phenyl silver nitrate, which becomes black when warmed.

According to the literature, the lead alkyls immediately reduce silver nitrate; the authors' hypothesis, that very unstable silver alkyls are formed as intermediate products, is confirmed by the observation that yellow precipitates are formed, which are stable at  $-30^{\circ}$  for several seconds, and at  $-80^{\circ}$  for several minutes.

H. W.

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## Physiological Chemistry.

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**Analyses of Blood Gases. III. The Permeability of Human Erythrocytes to Chlorions.** H. STRAUB and KLOTHILDE MEIER (*Biochem. Zeitsch.*, 1919, **98**, 205—228. Compare A., 1919, i, 53).—Blood corpuscles suspended in a physiological sodium chloride solution were subjected to the influence of various concentrations of carbon dioxide. It was found that the corpuscles acted as "buffers" towards carbon dioxide. The hydrion concentration of the inside of the cells exceeded  $P_H=7.00$  only when the sodium chloride solution in which the corpuscles were suspended reached an hydrion concentration of  $P_H=6.67$ . This is, no doubt, brought about by the alteration in the colloidal condition of the cell membrane. The change in the hydrion concentration was found to be independent of the concentration of Cl and Na ions of the solution in which the corpuscles are suspended as long as a certain minimum of these ions was assured and the solution made isotonic. In hypertonic 0.2 molar salt solutions, the change in the corpuscles was brought about at the same hydrion concentration, namely,  $P_H=6.67$ . In a hypertonic 0.102 molar solution, on the other hand, the change took place earlier.  
S. S. Z.

**Analyses of Blood Gases. IV. The Influence of Alkali Ions on the Hæmoglobin and Cell Membrane.** H. STRAUB and KLOTHILDE MEIER (*Biochem. Zeitsch.*, 1919, **98**, 228—256).—The influence of alkali ions on the electrical charge of hæmoglobin and on the permeability of the membrane of human erythrocytes to these ions has been studied. The membrane becomes permeable to the various ions at the following hydrion concentrations: Li and Na at  $P_H=6.67$ , K at  $P_H=6.8$ , Rb at  $P_H=6.92$ , Cs at  $P_H=7.06$ . The hæmoglobin loses its charge on the addition of the alkali ions



at the following hydron concentrations: Na and K at  $P_H=7.00$ , Rb at  $P_H=7.22$ , Cs at  $P_H=7.34$ . The membrane becomes permeable to ammonium ions in low concentrations at  $P_H=7.48$ . Higher concentrations of these ions require a higher hydron concentration before the membrane becomes permeable to them. The action of ammonium ions on the charge of the hæmoglobin is similarly influenced by the concentration of the ions. The analogy between the permeability of the cell membrane to the alkali ions, and the precipitation of colloids by means of these ions, is pointed out. The bearing of the adsorption theory on the permeability of the cell membranes to alkali ions is also discussed. S. S. Z.

**Influence of High Temperatures and Dilute Alkalis on the Antineuritic Properties of Food.** AMY L. DANIELS and NELLIE I. MCCLURG (*J. Biol. Chem.*, 1919, **37**, 201—213).—The results obtained by these authors are not in accord with those reported by McCollum and Simmonds (*ibid.*, 1918, **33**, 55). It appears improbable that the commercial canning of foods is responsible for a serious destruction of the antineuritic vitamine, and the warning sounded by Chick and Huma (*Proc. Roy. Soc.*, 1917, [B], **90**, 60) is regarded as unfounded. J. C. D.

**The Vitamines of Green Foods.** THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (with co-operation of EDNA L. FERRY and ALFRED J. WAKEMAN) (*J. Biol. Chem.*, 1919, **37**, 187—200).—Dried yeast is somewhat more than four times as efficient as dried spinach leaves when used as a source of the water-soluble vitamine. These leaves, however, appear to be a rich source of fat-soluble A. The values of cabbage, lucerne, clover, and timothy plants in supplying the water-soluble accessory substance are of the same order as that of spinach, but the experiments are not regarded as complete.

Very small amounts of lucerne, clover, and timothy plants will supply sufficient fat-soluble A for the growth of young rats. Emphasis is therefore laid on the importance of fresh green vegetables in the human dietary. J. C. D.

**Identity of the Water-soluble Growth-promoting Vitamines and the Antineuritic Vitamine.** H. H. MITCHELL (*J. Biol. Chem.*, 1919, **40**, 399—413).—The author reviews the literature dealing with the distribution, properties, and character of these two substances, and forms the opinion that there is as yet insufficient evidence to assume that they are identical. J. C. D.

**Formation of Urea by the Placenta.** FREDERICK S. HAMMETT (*J. Biol. Chem.*, 1919, **37**, 105—112).—Formation of urea by the placenta may be conclusively demonstrated, although the processes leading up to its production can only be surmised. J. C. D.

**Physical Properties and Chemical Composition of Human Amniotic Fluid.** DOKO UYENO (*J. Biol. Chem.*, 1919, **37**, 77—101).—The human amniotic fluid at the end of pregnancy

always contains coagulable albumins (an average of 0.226%, inclusive of mucin). The quantity of mucin was too small to be estimated. Peptones and proteoses were not found. Approximately 0.003% of ammonia and 0.0323% of urea were found, together with very small amounts of uric acid and creatine, but creatinine and hippuric acid were absent. Cholesterol is also a component of the human amniotic fluid. J. C. D.

**The Effect of Pyretics and Antipyretics on Catalase Production.** W. E. BURGE (*J. Pharm. expt. Ther.*, 1919, 14, 121—130).—Tetrahydro- $\beta$ -naphthylamine, adrenaline, caffeine, and sodium chloride stimulate the alimentary glands, particularly the liver, to an increased output of catalase; this fact is offered in explanation of the increased oxidation produced by these substances, and hence of the accompanying fever, in so far as the increased heat production is involved in this. Chloroform decreases catalase both by decreasing its output from the liver and by direct destruction of this enzyme. Ether decreases catalase principally by direct destruction of the enzyme without disturbing the liver function so much as does chloroform. Acetanilide, quinine, and phenacetin produce a slight decrease in catalase by decreasing its output from the liver. Chloroform and ether lower temperature in so far as decreased oxidation is involved in this by decreasing catalase, the enzyme principally responsible for oxidation in the body. The fact that acetanilide, quinine, and phenacetin have little or no effect in decreasing catalase suggests that their mode of action in lowering temperature is not due to a decrease in oxidation. J. C. D.

**The Carnosine Content of Normal and Pathological Human Cardiac Muscles.** F. BUBANOVIĆ (*Biochem. Zeitsch.*, 1918, 92, 125—129).—The carnosine content of the human heart is very constant, and is not influenced either by hypertrophy or atrophy of the muscles. The average content is 0.25%. The carnosine was determined when possible, both by the diazo and the copper colorimetric methods. S. S. Z.

**Bioluminescence. X. Production of Carbon Dioxide during Luminescence of Cypridina Luciferin.** E. NEWTON HARVEY (*J. Gen. Physiol.*, 1919, 2, 133—135).—All luminous animals require oxygen for luminescence, but there has previously been some doubt as to whether carbon dioxide is given off as a result of this phenomenon. A brilliant luminescence results when a small amount of luciferase solution is added to a solution of *Cypridina* luciferin (A., 1919, i, 299), so that it should be possible to ascertain whether this process is accompanied by a liberation of carbon dioxide. The results of experiments indicate that the oxidation of luciferin which is responsible for luminescence is not to be compared with the reactions in cells giving rise to the carbon dioxide of respiration. As previously suggested by the author, the process is probably similar to the oxidation of a leuco-dye (A., 1919, i, 299). J. C. D.

**Bioluminescence. XI. Heat Production during Luminescence of Cypridina Luciferin.** E. NEWTON HARVEY (*J. Gen. Physiol.*, 1919, 2, 137—143).—The heat change during the oxidation of luciferin by luciferase was investigated in order to ascertain the nature of the luminescent reaction. The change observed was so small that it is estimated that 1 gram of luciferin develops less than 0.1 cal. during the oxidation process accompanying luminescence. This clearly differentiates this type of reaction from those such as the oxidation of dextrose, 1 gram of which will give 4000 cal. It therefore appears probable that no carbon dioxide is produced during the oxidation of luciferin, and that the process is one more closely resembling the oxidation of leuco-methylene-blue (compare preceding abstract). J. C. D.

**Physiology of Phosphorus and Calcium Metabolism as Related to Milk Secretion.** EDWARD B. MEIGS, N. R. BLATHERWICK, and C. A. CARY (*J. Biol. Chem.*, 1919, 37, 1—75).—Normal blood plasma contains no phosphorised protein, and probably no phosphorus compounds other than phosphatides and inorganic phosphates. The phosphorus of these two classes of compounds certainly comprises more than 97% of all that exists in normal plasma. The precursor in plasma of milk fat and milk phosphorus is of a phosphatide nature. The concentration of calcium in the plasma of cows is quite constant. Small variations can be induced by varying the amount supplied with the rations, but the chief controlling factor is probably the concentration of bicarbonate in the plasma. It is probable that the concentration of calcium tends to vary inversely with that of the bicarbonate. The concentrations of phosphatide and inorganic phosphates in the plasma are highly variable. Both can be made to vary by changing the amount of phosphorus supplied with the rations, though the variations induced in this manner show themselves most markedly in the inorganic phosphate. Both undergo variations as the accompaniment of increasing age and of the later stages of pregnancy. The phosphatide of the plasma shows a marked tendency to rise during the first month of lactation, and to remain high until lactation has ceased. This phenomenon is largely independent of the diet, and is thought to be connected with the fact that near the beginning of lactation there is a tendency for the body fat to be released from its stores and thrown out into the blood.

J. C. D.

**Pyrrole and Melanuria.** PIETRO SACCARDI (*Atti R. Accad. Lincei*, 1919, [v], 28, ii, 85—89).—Administration of pyrrole leads to the formation of melanin in the urine in the case of the rabbit, but not in that of the dog; the latter, being essentially a carnivorous animal, appears easily to oxidise those products of the scission of proteins which lead to the formation of pyrrole, whereas with herbivorous animals the oxidation proceeds only as far as melanogen. Melanins have been obtained from rabbits' urine, from cuttle-fish, from black hair, from the choroid, and from a melanotic tumour,

the properties and reactions of the different products being described. These melanines all resemble closely pyrrole-black obtained by the chemical oxidation of pyrrole; when heated in a test-tube, they yield crystalline sublimates in the form of black, orthorhombic lamellæ, whereas precipitation of the melanines gives amorphous masses.

The glandular oxidation of pyrrole in aqueous suspension containing a few drops of toluene has been studied in vitro at about 40°, the glands used being the mamma, liver, testicles, thyroid, kidneys, and spleen of the ox. The glandular tissue gradually turns brown, and assumes the appearance of an ordinary melanotic tumour; the most intense blackening is shown by the liver and spleen, the testicles, kidneys, and thyroid following in order. The mamma exhibits no blackening after six days, and even undergoes putrefaction, in spite of the presence of toluene. Addition of adrenaline accelerates the blackening of the glandular organs.

T. H. P.

### **The Physical Theory of the Action of Drugs and Poisons.**

I. TRAUBE (*Biochem. Zeitsch.*, 1919, **98**, 177—197).—A theoretical paper. The pharmacological action of drugs and toxins is attributed mainly to their physical properties. It is urged that more attention ought to be given to the physical side of these principles in the study of chemotherapy.

S. S. Z.

### **The Biological and Pharmacological Properties of Chlorophyll.**

EMIL BÜRGI and C. F. VON TRACZEWSKI [with (FRL.) SCHEINA BASS, A. BRAUNSTEIN, and (FRL.) S. FRIDKISS] (*Biochem. Zeitsch.*, 1919, **98**, 256—284).—The hæmoglobin-forming capacity of chlorophyll was studied in a series of experiments in which the latter was administered to rabbits made anæmic by means of bleeding and by the action of phenylhydrazine. It was found that chlorophyll, as well as iron, when given in large doses possessed a blood-forming capacity. Both chlorophyll and iron were equally effective, whether the experimental anæmia was induced by bleeding or by the administration of phenylhydrazine. Small doses of chlorophyll were found to possess a "sensitising" effect on the action of iron in the production of blood.

S. S. Z.

### **Blood-forming Properties of Chlorophyll.**

R. GRIGORIEW (*Biochem. Zeitsch.*, 1919, **98**, 284—294).—Chlorophyll in the form of phæophytin possesses a higher blood-forming capacity than iron when given to normal or naturally anæmic rabbits. The best results are achieved with these animals by the administration of a combination of iron and chlorophyll.

S. S. Z.

### **Maximum Production of Glutamine by the Human Body as Measured by the Output of Phenylacetylglutamine.**

CARL P. SHERWIN, MAX WOLF, and WILLIAM WOLF (*J. Biol. Chem.*, 1919, **37**, 113—119).—No marked increase in sulphur metabolism

followed the ingestion of phenylacetic acid by man. This does not agree with the experimental results of E. and H. Salkowski working with rabbits (A., 1879, 662). Intestinal putrefaction, as measured by the excretion of ethereal sulphates, is decreased after administration of phenylacetic acid. About half of the acid administered was excreted in combination with glutamine.

J. C. D.

**Comparative Metabolism of certain Aromatic Acids. III. Fate of *p*-Nitrophenylacetic Acid in the Organism of Fowl, Dog, and Man.** CARL P. SHERWIN and MAX HELFAND (*J. Biol. Chem.*, 1919, **40**, 17—27).—The human organism eliminated 68·7% of the ingested *p*-nitrophenylacetic acid in the urine in the unchanged condition. Attention is drawn to the peculiar fact that this acid, although toxic to the body, is excreted without having been rendered innocuous by combination with some substance, such as glycine, in its passage through the tissues. When administered to the dog, the greater part is excreted unchanged, but some is found to be present in the urine as *p*-nitrophenylaceturic acid. In the case of the fowl, a certain amount of the *p*-nitrophenylacetic acid is excreted unchanged, but the greater part is combined with ornithine in the body and excreted as *p*-nitrophenylacetylornithinic acid,  $C_{21}H_{22}O_8N_4$ , short, thick, irregular needles, m. p. 184—185°.

J. C. D.

**Behaviour of Sudan III in the Animal Organism.** B. E. READ (*J. Biol. Chem.*, 1919, **37**, 121—135).—Sudan III dissolved in oil and administered intraperitoneally, subcutaneously, or by the mouth is absorbed, and may be traced in the lymph, blood, and bile. It is transported to the fatty tissue of the body, being deposited particularly in the omentum. It is excreted in the fæces, and is not found in the urine of normal animals. Ordinary commercial preparations of Sudan III contain more or less impurity of a toxic nature. The foreign substances are excreted in the urine, which is deeply coloured, and may cause death. J. C. D.

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## Chemistry of Vegetable Physiology and Agriculture.

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**The Catalase of Bacteria. II.** MARTIN JACOBY (*Biochem. Zeitsch.*, 1918, **92**, 129—139. Compare A., 1918, i, 517).—The bacterial catalase obtained by the author obeys the same reaction laws as catalases already studied. S. S. Z.

**Acidity Relationships of True Lactic Acid Bacteria.** OLOF SVANBERG (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 2, 1—10).—The author has investigated the acidity conditions

under which various micro-organisms can ferment milk and under which they can continue to grow. The change in the acidity of milk and whey by *Streptococcus lactis* has been ascertained at 16° and 37°, both by titration with *N*/10-sodium hydroxide and by Sørensen's method. At 16°, the  $P_H$  value in both cases is the same, 4.0, but the titration values are very different. *Bacterium casei*  $\epsilon$ , in milk and wort at 35° raises the acidity to  $P_H=3.05$ . If a pure *S. lactis* culture is placed in milk and allowed to act until the maximum acidity is reached, and the acidity is neutralised by alkali, the coccus will again produce acid, but the final concentration will be less than before, and this will be continued if the process of alternate fermentation and neutralisation is continued. The final acidity value is reduced by the addition of sodium lactate to milk proportionally to the lactate concentration. The acid tolerance of *S. lactis* is determined for sulphuric acid, hydrochloric acid, and phosphoric acid, and the same value found in each case, namely,  $P_H=3.4$  at 18°; in the case of *B. casei*  $\epsilon$ , the acid tolerance is found to be  $P_H=3.0$  at 35° for hydrochloric acid and phosphoric acid. The alkali tolerance of *S. lactis* at 18° lies at  $P_H=8$ .

J. F. S.

**The Surface Action of the Homologues of Hydroquinone and their Toxins.** I. TRAUBE (*Biochem. Zeitsch.*, 1919, 98, 197—205).—The hydrocupreines and their homologues show a parallelism between their disinfecting power against many bacilli and cocci, mostly gram-positive organisms, and their surface action. An analogy also exists between the susceptibility of bacteria towards basic stains and their power of adsorption of hydrocupreines and their toxins.

S. S. Z.

**Gentian-violet, its Selective Bactericidal Action.** M. L. CROSSLEY (*J. Amer. Chem. Soc.*, 1919, 41, 2083—2090).—Gentian-violet is a mixture of dextrin and dye in almost equal proportions, the dye being a mixture consisting chiefly of hexamethylparosaniline hydrochloride and pentamethylparosaniline hydrochloride with small amounts of the tetramethyl compound and lower homologues.

The selective bactericidal action of gentian-violet is no greater than that of its component dyes, and gentian-violet has no advantage over these in selective or differentiating power. Organisms which were gentian-positive were also gram-positive, the structure of the dye and of the organism being important factors in the selective action. The concentration of the dye is an important factor in determining its power to kill an organism. Not one of the dyes examined was effective for *B. subtilis* in dilutions greater than 1 in 100,000. *B. mycoides* was, however, killed by malachite green in dilution of 1 in 100,000, by rosaniline in dilution of 1 in 200,000, and by gentian-violet, or either of its two principal components, in dilution of 1 in 300,000. The basic nitrogen groups appear to be the reactive groups, and their action is intensified by substitution of methyl for amino-hydrogen.

W. G.

**The Influence of Potassium Salts on the Enzyme of *Aspergillus Oryzæ* which Liquefies Starch.** GEN-ITSU KITA (*Mem. Coll. Eng. Kyoto*, 1918, **2**, 1).—Potassium salts promote the property of the enzyme to liquefy starch even when the saccharification is retarded. On the addition of suitable quantities of these salts to the mash no blue coloration is obtained with iodine after the fermented wort is boiled. This reaction, according to the author, is usually present when these salts are not added. The above facts are of technical significance. S. S. Z.

**Formation of Acids by Moulds and Yeasts. II.** FRIEDRICH BOAS and HANS LEBERLE (*Biochem. Zeitsch.*, 1918, **92**, 170—188. Compare A., 1919, i, 508).—The formation of acids by *Mycoderma*, *Oidium*, and *Aspergillus niger* in media containing various carbohydrates and nitrogenous ingredients has been studied. The greater part of the acid is formed from the carbohydrate. When, however, an ammonium salt of a strong acid forms the source of nitrogen, the liberated acid suppresses the formation of acid from the carbohydrate. The ammonia formed in the fermentation process from the various nitrogenous compounds by means of enzymic action greatly influences the formation of acid. This is dependent on the character of the organism and the nature of the carbohydrate employed. S. S. Z.

**Natural and Artificial Formation of Glycerol in Alcoholic Fermentation.** CARL NEUBERG and ELSA REINFURTH (*Biochem. Zeitsch.*, 1918, **92**, 234—267).—By employing sodium sulphite as "fixing" agent for the acetaldehyde formed in alcoholic fermentation an equivalent amount of glycerol is also formed. More than 70% of the theoretical amount of acetaldehyde is thus fixed. The amount of acetaldehyde and glycerol produced increases with the amount of sulphite employed. Acetaldehyde and glycerol are therefore not only by-products, but are produced in considerable quantities in certain stages of alcoholic fermentation. S. S. Z.

**Autolysis of Yeast in its Dependence on Hydrogen and Hydroxyl-ions.** K. G. DERNBY (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 23, 1—26).—On the basis that enzymes are amphoteric electrolytes, the author has examined the autolysis of yeast at various temperatures in the presence of electrolytes. It is shown that the simple yeast cell contains enzymes which are capable of degrading albuminous substances. These enzymes are analogous in type with those present in specific animal organs. The enzymes identified in the paper are (a) yeast pepsin, which degrades albuminous substances to peptones, and has a maximum activity at  $P_H=4-4.5$ , (b) yeast tryptase, which does not attack the yeast albumin, but destroys gelatin, casein, Witte-peptone, and similar substances, and has a maximum activity at  $P_H=7.0$ , (c) yeast eriptase, which degrades polypeptides to amino-acids and has a maximum activity at  $P_H=7.8$ . The autolysis of yeast is brought about by these enzymes and consists in a successive degradation of



albumin; it can only proceed when the different enzymes can operate simultaneously. The best hydrogen-ion concentration for the process is  $P_{\text{H}}=6.1$ , which lies between that of yeast tryptase and yeast pepsin. J. F. S.

**Extraction and Concentration of the Water-soluble Vitamine from Brewer's Yeast.** THOMAS B. OSBORNE and ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1919, **40**, 383—394).—By precipitation of a dilute acetic acid extract of yeast with alcohol the authors have succeeded in obtaining a fraction which appears to contain a very large proportion of the water-soluble accessory substance present in the original yeast. The chemical nature of the substances in this fraction is not yet determined. J. C. D.

**Examination of the Urease-content of Indigenous Seeds.** D. H. WESTER (*Chem. Weekblad*, 1919, **16**, 1548—1551).—The urease content of a large number of seeds was determined. It varied from nil or very small amounts up to a considerable quantity in the laburnum. Plants of the same natural order differ widely in regard to the urease content of their seeds. In no case did the amount of urease approach that found in soja beans or canavalia beans, and of these the latter contained approximately ten times as much urease as the former. W. J. W.

**Do Seedlings Reduce Nitrates?** J. DAVIDSON (*J. Biol. Chem.*, 1919, **37**, 143—148).—The author reaches the conclusion that growing seedlings do not, as part of their metabolic processes, reduce the nitrates in the outside medium in which they are growing. J. C. D.

**Complex Iron Salts. I.** OSKAR BAUDISCH (*Biochem. Zeitsch.*, 1918, **92**, 189—198).—In mixed aqueous solutions of ferric chloride and formaldoxime, phloroglucinol, catechol, or resorcinol exposed to the air, trivalent iron is slowly reduced to its bivalent form in the presence of dilute hydrochloric acid. Similarly, in admixed solutions of ferric chloride and quinol, acetylacetone, acetoacetic ester, salicylaldehyde, salicylic acid, and catechol-*o*-carboxylic acid, the above reduction is only effected after exposure to the rays of a mercury quartz lamp or sunlight. Aqueous solutions of ferric chloride and dimethylglyoxime, on the other hand, are not reduced even after exposure to the light. The chemistry of these observations and their bearing on some physiological phenomena of the plant are discussed. S. S. Z.

**Presence in Plants of Hæmatoid Iron Compounds. III.** G. GOLA (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 146—150).—Experiment indicates that the peroxydasic function in plants is due in most cases, not only to true enzymes, but also to various iron compounds. The latter are probably catabolic products of more complex compounds, such as the hæmatoids, which largely form incrustations on the cellular membranes, and are, in virtue of their

physical state, able to act between the oxidisable substances and the peroxides.

T. H. P.

**Position and Osmotic Pressure.** O. ARRHENIUS (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, 5, No. 15, 1—20).—A discussion of the relation between the osmotic pressure of the cell sap and the position of plants and trees. By "position" is meant, not only the geographical position, but also the factors, such as light, heat, moisture, winds, composition of the substratum, etc., which affect the growth of the plants.

T. S. P.

**The Isoelectric Points of the Proteins in certain Vegetable Juices.** EDWIN J. COHN, JOSEPH GROSS, and OMER C. JOHNSON (*J. Gen. Physiol.*, 1919, 2, 145—160).—The hydrogen-ion concentration of filtered potato juice is approximately  $10^{-7}N$ . The isoelectric point of tuberin, the chief protein of the potato, determined by the cataphoresis method, is at a hydrogen-ion concentration slightly lower than  $10^{-4}N$ . At acidities greater than the isoelectric point, tuberin exists combined with acid. The isoelectric point of the protein in carrot juice coincided with that of tuberin, and the properties of carrot juice and potato juice were found to be remarkably similar.

The protein of the tomato existed in a precipitated form near its isoelectric point. Accordingly, it was not present to any extent in filtered tomato juice. If, however, the considerable acidity of the juice was neutralised, the protein dissolved and was filterable. The addition of sufficient acid to make the hydrogen-ion concentration slightly greater than  $10^{-5}N$  again precipitated the protein at its isoelectric point.

J. C. D.

**Fat-soluble Vitamine. II. The Fat-soluble Vitamine Content of Roots, together with some Observations on their Water-soluble Vitamine Content.** H. STEENBOCK and E. G. GROSS [with M. T. SELL] (*J. Biol. Chem.*, 1919, 40, 501—531).—In the plant kingdom, the occurrence of the fat-soluble vitamine cannot always be associated with a preponderance of actively functioning cells, as distinguished from those that serve primarily as storage organs. Thus the sweet potato is rich in this accessory factor, whilst the ordinary potato contains very little; similarly, in the case of the roots, carrots contain much of the vitamine, but beets and mangels do not.

In the case of the water-soluble vitamines, the carrot, rutabaga, and dasheen contain more than do sugar-beets and mangels.

J. C. D.

**Reducing Action of Roots of the Graminaceæ: Reduction of Calcium Nitrate. I. and II.** GIOVANNI SANI (*Atti R. Accad. Lincei*, 1919, [v], 28, ii, 199—201, 244—247).—When the roots of wheat, maize, and oats, gathered at the beginning of the flowering period, are pounded in a mortar and then extracted with boiling water, liquids are obtained which exert pronounced reducing action

on Fehling's solution. The pulped roots, which have an acid reaction, are also able, in the cold, to reduce calcium nitrate, this reduction being inhibited by the presence of alkaline Rochelle salt solution. The reduction of calcium nitrate proceeds only to a definite limit, and then ceases entirely, the product of the reduction apparently acting as a poison towards the reducing agent; in the plant itself, however, such poisoning action would not occur, utilisation of the reduction product preventing its accumulation. The nature of this reduction product has not yet been established.

T. H. P.

**Globulin of the Coconut, *Cocos nucifera*. I. Preparation of Coconut Globulin. Distribution of the Basic Nitrogen in Coconut Globulin.** CARL O. JOHNS, A. J. FINKS, and C. E. F. GERSDORF (*J. Biol. Chem.*, 1919, **37**, 149—153).—The globulin contains the following amounts of basic amino-acids: cystine, 1.44%; arginine, 15.92%; histidine, 2.42%; lysine, 5.80%. Tryptophan is present. The free amino-nitrogen was found to equal nearly one-half of the lysine nitrogen.

J. C. D.

**Globulins of the Jack Bean, *Canavalia ensiformis*.** JAMES B. SUMNER (*J. Biol. Chem.*, 1919, **37**, 137—142).—Two crystalline globulins and one non-crystalline globulin have been isolated from the jack bean. *Concanavalin B* crystallises in needles, slowly soluble in 10% sodium chloride, soluble in excess of alkali; *concanavalin A* crystallises in bisphenoid form, insoluble in any but concentrated salt solutions; canavalin, the uncrystallisable globulin, is readily soluble in 1% sodium chloride solution (compare Jones and Johns, A., 1917, i, 191).

J. C. D.

**Examination of the Urease-content of Soja Beans from Various Sources.** D. H. WESTER (*Chem. Weekblad*, 1919, **16**, 1552—1556).—Nearly all the varieties examined showed a high urease content, and this was not diminished by age. The lowest enzymic action was found in soja beans from the Cameroons and Germany, which raises an interesting question in regard to diminution of effectiveness brought about by transferring the plant from its original habitat, Asia.

W. J. W.

**A Quantitative Relation between Soil and the Soil Solution brought out by Freezing-point Determinations.** BERNARD A. KEEN (*J. Agric. Sci.*, 1919, **9**, 400—415).—Bouyoucos and his co-workers, by determinations *in situ* of the freezing-point depression of soil solution, at varying moisture contents, have shown that the soil solution in quartz sand and extreme types of sandy soil obeys approximately the same law as dilute solutions, but that the soil solutions of ordinary soils do not obey this law (compare *J. Agric. Sci.*, 1914, **6**, 456). Bouyoucos assumes that some of the soil water is rendered unfree in the sense that it does not take part in the depression of the freezing point. The present author, accept-

ing the truth of this assumption, and using some of Bouyoucos's data, has shown that the water rendered unfree is not a constant amount, but varies with the total moisture content. A definite relation exists between the free, unfree, and total moisture expressed by the equations  $Y_n = cM_n^x$  and  $Z_n = Y_n^{1/x} / c^{1/x} - Y_n$ , where  $c$  and  $x$  are constants for any one soil, and  $M_n$ ,  $Y_n$ , and  $Z_n$  represent respectively the total, free, and unfree water. Over the experimental range the ratio of free to total water continually decreases, and that of unfree to total water continually increases as the total moisture diminishes in amount. The constant  $c$  contains an unknown factor, namely, the quantity of free water at the highest amount of total water used in the experiments, and according to the value arbitrarily assigned to it so the amount of unfree water may continually decrease with decrease of total moisture over the experimental range or may increase to a maximum and then decrease. The same general conclusions on the relations existing between the soil and its moisture constant as were drawn from the author's experiments (compare *loc. cit.*) on the evaporation of water from soil, again follow.

W. G.

### Soil Acidity, the Resultant of Chemical Phenomena.

H. A. NOYES (*J. Ind. Eng. Chem.*, 1919, **11**, 1040—1049).—Chemical reactions are held to be the cause of soil acidity. The presence of free hydrogen ions in the soil extract is considered to be due to hydrolysis. As regards the action of organic matter, physicochemical explanations of the hydrolysis of silicates and of organic matter and the ability of organic matter to form complex ions with bases are more satisfactory than are "adsorption" theories. The reaction of a soil at any time depends on the nature of its constituents and the proportions in which they are present with water. Change in the water content, removal of substances from solution, and the addition of other substances, all alter the reaction of the soil in accord with the law of mass action.

W. P. S.

**The Richness in Copper of Cultivated Soils.** L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1919, **169**, 937—942).—The authors have not estimated the total copper, but the amount which is dissolved when 6 grams of the soil are boiled very gently for half an hour with 50 c.c. of 10% sulphuric acid. Arable soils contain very little copper, the amount varying, in the soils examined, from 1 to 50 mg. per kilogram of soil, but in the case where the high figure was obtained the soil had carried crops which had frequently been treated with copper sulphate. In the case of vineyard soils, where it was known that the vines had been treated with copper sulphate over a long period of years, the copper content rose to as high as 250 mg. per kilo. of soil. The copper was almost entirely found in the surface layer of the soil, the penetration being extremely slow. Despite the high copper content of some of these soils, there was no indication of any toxic effect on the vines.

W. G.

**The Amount and Composition of Rain Falling at Rothamsted (Based on Analyses made by the late Norman H. J. Miller).** E. J. RUSSELL and E. H. RICHARDS (*J. Agric. Sci.*, 1919, 9, 309—337).—A summary of the results of analyses of Rothamsted rain water made by the late N. H. J. Miller from 1888 to 1916. The rain water contained, on an average, 0.405 part per million of ammoniacal nitrogen, 0.204 part per million of nitric nitrogen, 2.43 parts per million of chlorine, and 10 parts per million of dissolved oxygen. Both the yearly and monthly fluctuations of ammoniacal nitrogen move in the same direction as the rainfall, the general level being highest in May, June, July, and August, and lowest in January, February, March, and April. Up to 1910 the nitric nitrogen fluctuated in amount year by year and month by month in the same way as the ammoniacal nitrogen, but since that date there has been no simple relationship. The fluctuations of the chlorine content of the rain closely follow the rainfall, but the general level is much higher during the months September to April than during the summer months.

The sources of ammonia in the rain are given as the sea, the soil, and city pollution; the soil is indicated as an important source by the fact that the ammonia content is high during periods of high biochemical activity in the soil, and low during periods of low biochemical activity. Further, the close relationship between the amounts of ammoniacal and nitric nitrogen suggests either a common origin or the production of nitric compounds from ammonia. It seems probable that the chlorine comes from the sea, but some may come from fuel.

During the period under examination there has been a rise in the amounts of nitric nitrogen and of chlorine in the rain, and a tendency for the ammonia content to drop. It is suggested, as a possible explanation, that some former source of ammonia is now producing nitric nitrogen; it is possible that modern gas-burners and grates tend to the formation of oxides of nitrogen rather than ammonia.

There is a marked difference in composition between summer and winter rain water, which suggests that these may differ in origin. The winter rain resembles Atlantic rain in its high chlorine and low ammonia and nitrate content; the summer rain is characterised by low chlorine but high ammonia and nitrate content, and it is suggested that it may arise by evaporation of water from the soil and condensation at higher altitudes than in the case of winter rain.

W. G.

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## Organic Chemistry.

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**Oxidation of Methane.** R. K. BAILEY (U.S. Pat. 1319748).—Methane or natural gas is mixed with twice its volume of nitric oxide and with sufficient oxygen or air to form nitrogen peroxide. This mixture is passed through a porcelain or other inert tube heated to redness. Oxidation products, including formaldehyde, are obtained. The oxidation is prevented from being carried too far by conducting the reaction products as quickly as possible into a cooling chamber, where they are brought into contact with a sludge of calcium carbonate, which unites with the oxides of nitrogen, except nitric oxide. Formaldehyde is recovered from the solution after separating the solids from the sludge. Instead of using calcium carbonate, the hot reaction gases may be brought into contact with calcium oxide to effect absorption of water, thus preventing formation of nitrous and nitric acids, which if present would oxidise the formaldehyde. Reaction temperatures as low as 450° may be employed.

CHEMICAL ABSTRACTS.

**Methyl Sulphate.** T. H. DURRANS (U.S. Pat. 1317648).—Methyl sulphate is produced, together with methyl hydrogen sulphate and methyl chloride, by treating methyl alcohol, preferably with cooling, with chlorine and sulphur dioxide, the latter preferably being in slight excess throughout the reaction. Methyl chloride is removed by distillation at the ordinary pressure and the methyl sulphate under reduced pressure, or the products may be used together as alkylating agents.

CHEMICAL ABSTRACTS.

**Improvements in the Manufacture of Aliphatic Nitrites.** PAUL RENE DE WILDE (Brit. Pat. 133304).—Nitrites of aliphatic alcohols are produced by the reducing action of sulphur dioxide on solutions of the alcohols in pure or diluted nitric acid, or, alternatively, a saturated alcoholic solution of sulphur dioxide may be mixed with nitric acid. As an example, 74 grams of *isobutyl* alcohol dissolved in 100 grams of nitric acid (D 1.375) yield on treatment with sulphur dioxide 85 grams of *isobutyl* nitrite.

G. F. M.

**Preparation of Chloromethyl Carbonates.** ANDRÉ KLING, D. FLORENTIN, and E. JACOB (*Compt. rend.*, 1920, 170, 111—113. Compare this vol., i, 139, and Grignard, Rivat, and Urbain, this vol., i, 139).—By the successive chlorination of methyl carbonate, mono-, di-, tri-, tetra-, penta-, and hexa-chloro-derivatives are obtained, the most symmetrical derivative being obtained in each case.

W. G.

**Properties of the Chloromethyl Carbonates.** ANDRÉ KLING, D. FLORENTIN, and E. JACOB (*Compt. rend.*, 1920, 170, 234—236).—The physical properties of the nine possible chlorinated

methyl carbonates, the preparations of which have previously been described (preceding abstract), are given, as below:

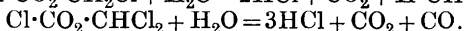
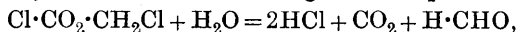
Formula.	M. p.	B. p./760 mm.	B. p./50 mm.	D <sup>15</sup> .
CH <sub>2</sub> Cl·O·CO <sub>2</sub> Me ...	—	139—140°	67°	1·303
CO(O·CH <sub>2</sub> Cl) <sub>2</sub> ...	—	176°	99°	1·480
CHCl <sub>2</sub> ·O·CO <sub>2</sub> Me ...	—	147°	72°	1·421
CHCl <sub>2</sub> ·O·CO <sub>2</sub> ·CH <sub>2</sub> Cl ...	—	178°	102°	1·562
CCl <sub>3</sub> ·O·CO <sub>2</sub> Me ...	— 70° (viscous)	165°	86°	1·535
CO(O·CHCl <sub>2</sub> ) <sub>2</sub> ...	— 40°	182—183°	105—106°	1·618
CCl <sub>3</sub> ·O·CO <sub>2</sub> ·CH <sub>2</sub> Cl ...	— 70° (viscous)	150° (decomp.)	110°	1·631
CCl <sub>3</sub> ·O·CO <sub>2</sub> ·CHCl <sub>2</sub> ...	— 30°	196°	115°	1·686
CO(O·CCl <sub>2</sub> ) <sub>2</sub> ...	78°	203°	124°	—

The substances which contain the group ·O·CCl<sub>3</sub> are particularly toxic.

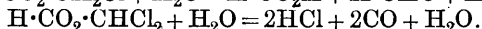
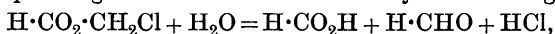
W. G.

**Organic Derivatives of Tellurium. I. Dimethyl-tellurium Dihaloids.** RICHARD HENRY VERNON (T., 1920, 117, 86—98).

**The Industrial Chloromethyl Formates and their Analysis.** MARCEL DELÉPINE (*Bull. Soc. chim.*, 1920, [iv], 27, 39—45).—The mono- and di-chloromethyl chloroformates are decomposed by dilute alkali according to the equations:



The corresponding mono- and di-chloromethyl formates give



The formaldehyde formed may be estimated by Romijn's method (compare A., 1897, ii, 166), the formic acid by Pean de St. Gilles's method (compare *Ann. Chim. Phys.*, 1859, 55, 374), and the carbon monoxide by direct measurement of its volume after decomposing the material with sodium hydroxide. These results, together with the percentage of chlorine, enable an idea to be formed as to the different esters present in industrial chlorinated methyl formates. [See, further, *J. Soc. Chem. Ind.*, 1920, 205A.]

W. G.

**Manufacture of Esters of Ethylenic Halogenhydrins.** SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat. 128911).—Ethylenic halogenhydrin esters of the general formula



where R is an alkyl or aryl group and X a halogen, are prepared by the interaction of ethylene oxide and an acidyl haloid in equimolecular proportions at a suitable temperature, depending on the particular acid chloride or bromide used. The reaction is conveniently brought about by passing gaseous ethylene oxide through the acidyl haloid at ordinary atmospheric pressure, and quantitative yields are obtained. Examples are given of the preparation of *β*-chloroethyl acetate, b. p. 143—144°, from acetyl chloride at its boiling point, *β*-chloroethyl chloroacetate, b. p. 94—95°/12 mm.,

from chloroacetyl chloride at 100°, *β*-chloroethyl benzoate, b. p. 120—122°/5 mm., from benzoyl chloride at 190—240°, *β*-chloroethyl *p*-nitrobenzoate, yellow crystals, m. p. 56°, from *p*-nitrobenzoyl chloride at 190—240°, and *β*-bromoethyl acetate, b. p. 163°, from a mixture of equimolecular proportions of ethylene oxide and acetyl bromide kept for several hours at the ordinary temperature.

G. F. M.

**Colloid-chemical Studies on Soaps. Non-aqueous Lyophilic Soap Colloids.** MARTIN H. FISCHER (*Chem. Eng.*, 1919, 27, 184—193).—The solvation capacities of various sodium soaps of the acetic series were determined. One gram-mol. of sodium arachidate will take up 27.5 litres of ethyl alcohol and still form a non-synergetic gel. The capacity of the lower members of the series becomes less as the molecular weight of the soap decreases. When a given soap is employed with different alcohols, the solvation capacity increases as the molecular weight of the alcohol becomes greater. The author has elaborated his theory of lyophilic and lyophobic colloids. The theory of soap gels is also dealt with. According to this, soaps form (*A*) true solutions in a solvent at higher temperatures. On the other hand, (*D*), a gel, when the temperature is low, is a true solution of the solvent in the solvated soap. Between these two extremes there exist two stages, (*B*) solvated soap dispersed in the solvent, (*C*) dispersed solvent in the solvated soap. If the temperature of *A* is lowered, all these stages are obtained. This is also true when the temperature of *D* is raised. The ranges of temperature in which *B* or *C* exists are not necessarily the same when the temperature of *A* is being lowered as when the temperature of *D* is being raised, because of a hysteresis effect. There exists, therefore, a region of ambiguity which depends on the previous history of the system. Gelation capacity is for these reasons not synonymous with solvation capacity. The latter is the phenomenon generally known as swelling, which is a different process from liquefaction.

CHEMICAL ABSTRACTS.

**Colloid-chemical Studies on Soaps.** MARTIN H. FISCHER and MARION O. HOOKER (*Chem. Eng.*, 1919, 27, 223—232. Compare preceding abstract.)—Solutions of sodium or potassium hydroxide of various concentrations are added to a standard aqueous solution of potassium oleate having the consistency of a syrup. As the concentration of the base is increased, the viscosity becomes greater until a gel is formed. Further addition of the base causes the soap to separate and the viscosity to fall rapidly. The separation of the soap occurs at a lower concentration for sodium hydroxide than for potassium hydroxide. The addition of aqueous ammonia always lowers the viscosity, the authors' explanation being that ammonium soaps are more soluble in water and are better solvents for water. Similar results are obtained when a sodium or potassium salt is added in place of the hydroxide, except that potassium acetate has a much greater salting-out effect than the chloride, nitrate, etc. Ammonium salts, on the other hand, emulsify the



soap, but do not salt it out. Calcium or magnesium salts form insoluble or less hydrated soaps, and therefore the viscosity steadily decreases as more of the salt is added. Salts of the heavy metals, such as copper or iron, cause the soap to separate in hard lumps. The effect is additive when potassium hydroxide or a potassium salt is also added.

CHEMICAL ABSTRACTS.

**Oleates and Stearates of certain Metals.** MATHEUS D'ANDRADE ALBUQUERQUE (*Revista Chim. pura appl*, 1916, [ii], 1, reprint, 8 pp.).—The oleates and stearates of a number of metals were prepared by double decomposition of solutions of their salts with alkali soaps. The ethereal solutions of some of the metallic soaps oxidised on exposure to air; the action of hydrogen peroxide on the ethereal solutions was also ascertained.

Metal.	Colour of ethereal solution.	Oxidation by air to—	Oxidation by $H_2O_2$ to—	Stability of peroxidised solution.
Ag'	colourless	—	pale yellow	—
Cu'	amber-yellow	bluish-green	—	—
Cu''	bluish-green	—	yellowish-brown	unstable
Hg'	colourless	—	no colour change	—
Hg''	colourless	—	no change	—
Mn''	almost colourless	—	dark chestnut	stable
Co''	red	dark green	dark green	stable
Pb''	colourless	—	orange-yellow	very unstable
Cr''	pink	violet	violet	—
Cr'''	violet	—	no change	—
V''	violet (?)	green (at once)	not given	—

Titanium soaps could not be obtained. The cuprous compounds were made from cupric soaps by reduction with hydrazine sulphate as well as by the action of alkali stearate and oleate on moist cuprous chloride. The silver compounds were darkened by light. By means of the ethereal soap solutions, it was possible to observe the absorption spectra of the various metals in the non-ionised state. The chromic compounds showed a strong absorption in the yellow.

W. R. S.

**[Preparation of] Maleic Acid from Benzoquinone by Catalytic Oxidation.** J. M. WEISS and C. R. DOWNS (U.S. Pat. 1318632).—Maleic acid is produced by dissolving benzoquinone in benzene and subjecting the mixture in the vapour phase to catalytic oxidation under conditions as described in U.S. Pat. 1318631 (this vol., i, 236). Inert diluent gases may be employed to control the reaction. In the condensate obtained from the reaction products there is usually present benzoquinone, maleic acid, benzene, formaldehyde, water, and various other by-products.

CHEMICAL ABSTRACTS.

**[Preparation of] Maleic Acid by Catalytic Oxidation of Benzene.** J. M. WEISS and C. R. DOWNS (U.S. Pat. 1318633).—The patent relates to a method of the same character as that described above (preceding abstract), preferably operating at 300–550°, with subsequent recovery of maleic acid as the main

product. When equal weights of benzene vapour and air are passed over vanadium oxide as a catalyst at such a velocity that the mixture stays in contact with the catalyst about 0.25 sec., a maximum yield of maleic acid is obtained by maintaining the catalyst at 400–450°.

CHEMICAL ABSTRACTS.

**The Mode of Pyrogenic Decomposition at High Temperature of Acetaldehyde, Metacetaldehyde, and Ethyl Alcohol.** (MLLE.) EGLANTINE PEYTRAL (*Bull. Soc. chim.*, 1920, [iv], 27, 34–39).—When acetaldehyde is submitted to a high temperature for a very short time, the main decomposition is its conversion into carbon monoxide and methane, the molecule thus undergoing the least deformation possible. A second reaction proceeding at the same time, but to a less extent, yields carbon monoxide, ethylene, and oxygen. If the time of heating is prolonged, other secondary products, such as acetylene and benzene, appear.

Metacetaldehyde, under similar conditions, is first depolymerised to give acetaldehyde, which then undergoes the changes given above. In the case of ethyl alcohol, the principal reaction is its oxidation to acetaldehyde, which then undergoes pyrogenic decomposition, as described. A second reaction proceeding simultaneously, but to a lesser extent, results in the conversion of the alcohol into ethylene and water.

W. G.

**A Keto-glycol Derived from Mesityl Oxide.** J. PASTUREAU and CH. LAUNAY (*Bull. Soc. chim.*, 1919, [iv], 25, 593–597).—The crystalline compound, m. p. 123°, obtained by Wolfenstein (compare A., 1895, i, 644) by the action of hydrogen peroxide on mesityl oxide, is shown to be not a glycol, as described by him, but a peroxide of mesityl oxide,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH} < \begin{smallmatrix} \text{O} \\ \text{CMe}_2\cdot\text{O} \end{smallmatrix}$ , and on hydrolysis it loses oxygen and gives the glycol of mesityl oxide described by Harries and Pappos (compare A., 1901, i, 673).

W. G.

**Lactose.** J. GILLIS (*Rec. trav. chim.*, 1920, 39, 88–125).—A more detailed account of work already published (compare A., 1918, i, 101, 155).

W. G.

**Lignin.** ERIK HÄGGLUND (*Arkiv. Kem. Min. Geol.*, 1918–1919, 7, No. 8, 1–20).—Reviewing the results of previous workers, the author attaches most importance to those of Klason (A., 1908, i, 717, and *Svensk Papperstidning*, 1916, No. 17), derived from a study of the ligninsulphonic acids; but the regeneration of lignin from these derivatives by means of 70% sulphuric acid, a method also used by Koenig (*Chem. Zeit.*, 1912, 36, 1101), requires one to two hours, and is accompanied by considerable decomposition of the lignin. The author now finds that 28% by weight of the wood of “hydrochloric acid–lignin” is obtained by shaking 1 part of finely powdered pine wood with 10 parts of 43% hydrochloric acid for fifteen minutes, rapidly filtering, and washing the residue free from hydrochloric acid. The product is a

pale brown powder with a strong odour of vanillin, and contains 1.63% of combined chlorine. It gives a deep purple colour with phloroglucinol in hydrochloric acid solution, a pale yellow colour with aniline sulphate, a dark red colour with *p*-phenylenedimethyldiamine sulphate, a dark blue colour with equal parts of potassium ferricyanide and ferric chloride, but no precipitate with Maule's reagent. A comparison of its methoxyl content with that of the original wood shows that about 20% of this is split off during the hydrochloric acid treatment. After introducing a corresponding correction, the author's analytical results agree with Klason's formula,  $(C_{40}H_{40}O_{11})_n$ , for lignin, but not with those of Cross and Bevan ("Cellulose," iii) or of Green (Schwalbe, "Chemie der Cellulose," 1911, 448). Protocatechuic acid was identified among the products of fusion of hydrochloric acid-lignin with potassium hydroxide and lead peroxide, but acetic acid, oxalic acid, and catechol could not be detected. The formation of these products from wood (Lange, A., 1890, 228) is therefore due to other constituents than lignin. The author also investigated his product in regard to its furfuraldehyde content, solubility in bisulphites and in alkalis, the action of chlorine and bromine, its oxidation with alkaline permanganate and with potassium chlorate and nitric acid, and the results of dry distillation.

J. K.

**Salts of  $\beta$ -Hydroxytrimethylenediglycine and of *N*-Hydroxymethylglycine.** HUGO KRAUSE (*Ber.*, 1919, 52, [B], 1211—1222).—The peculiarity (A., 1918, i, 156) attending the formation of the barium salt ( $+3H_2O$ ) of  $\beta$ -hydroxytrimethylenediglycine (the barium salt containing  $1.5H_2O$  [A., 1918, i, 337] is now stated to be non-existent) has been examined. It is due to supersaturation, which, however, is not always operative; in many experiments a noteworthy retardation of the crystallisation was never observed when technical formalin reacted with a freshly prepared solution of barium glycine or when a solution of the latter which had been kept in the cold for an hour or longer was treated with formaldehyde solution containing or not containing methyl alcohol. The initiation of crystallisation by the addition of a little methyl alcohol (*loc. cit.*) cannot be regarded, therefore, as a proof that the alcohol plays a part in the reaction.

A second *barium* salt of the same composition,



which is amorphous and extremely soluble in water, is obtained by treating a 25% solution of  $\beta$ -hydroxytrimethylenediglycine in formalin, which has been kept for a few days, with the theoretical quantity of a 15% paste of barium hydroxide, and adding 8 vols. of 80% methyl alcohol to the resulting, almost clear solution.

Some experiments on the simultaneous formation of the barium salts of  $\beta$ -hydroxytrimethylenediglycine and *N*-hydroxymethylglycine indicate that the production of the latter is favoured by working at low temperatures with pure formaldehyde, any considerable excess of which is to be avoided.

In addition to the salts of *N*-hydroxymethylglycine already described (*loc. cit.*; A., 1919, i, 67), the following have been prepared by the action of pure 33% formaldehyde solution on the metallic glycine salt: *potassium*,  $\text{OH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{K}$ , amorphous, brittle mass, which is obtained in a purer form by treating the normal lead salt with potassium sulphide; *sodium* (at  $80^\circ$  in a vacuum these two salts [2 mols.] appear to lose water [1 mol.], with the formation of anhydro-salts); *barium* ( $+2\text{H}_2\text{O}$ ), microscopic rods; *calcium* ( $+1\text{H}_2\text{O}$ ), hygroscopic, amorphous powder. The copper and lead salts must be dried over calcium chloride, not over sulphuric acid (*loc. cit.*), which causes loss, not only of water, but also of a little formaldehyde. C. S.

**Behaviour of Carbamide towards Hydrogen Peroxide and a Simple Process for its Purification and Decoloration.**

HERMANN KUNZ-KRAUSE (*Kolloid Zeitsch.*, 1919, 25, 240—241).—Carbamide is not affected in the slightest degree by boiling it in aqueous solution with hydrogen peroxide, but colloidal colouring matter, which is generally present in carbamide, is destroyed. Carbamide made from potassium cyanide which has been obtained from potassium ferrocyanide often exhibits a blue to green tint, which cannot be removed by recrystallisation. The colour is due to Prussian-blue, and is destroyed by boiling the carbamide with hydrogen peroxide. J. F. S.

**Carboalkyloxythiocarbamides.** AUGUSTUS EDWARD DIXON and RAYMOND THOMAS JOACHIM KENNEDY (*T.*, 1920, 117, 80—85).

**Preparation and Separation of Cyanates Soluble in Water.** J. D. RIEDEL (D.R.-P. 314629; from *Chem. Zentr.*, 1919, iv, 913).—Chlorine or bromine is directly added to highly concentrated alkaline solutions of cyanides; formation of cyanogen haloid only occurs to a subsidiary extent. Sodium cyanate is smoothly formed by this reaction, and is deposited in the solid state from its solution as the process goes forward. The product is applicable to technical and pharmaceutical purposes. H. W.

**Free Thiocyanogen.** ERIK SÖDERBÄCK (*Annalen*, 1919, 419, 217—322).—The author discusses the unsuccessful attempts of Liebig (1829 and 1844), Linnemann (1861), and Schneider (1866) to prepare thiocyanogen. Klason's compound,  $(\text{CN})_3\text{S}_3\cdot\text{S}_3(\text{CN})_3$ , obtained in 1886, is a cyanuric derivative. Quite recently, Bjerrum and Kirschner have detected small quantities of thiocyanogen in aqueous solutions of complex gold thiocyanates,  $\text{MAu}(\text{SCN})_4$ .

When an ethereal *N*- or *N*/10-solution of iodine is shaken with silver thiocyanate in excess, the colour of the iodine rapidly fades and yellow silver iodide is formed. The reaction, however, appears to reach a state of equilibrium. As it is impossible to separate completely the excess of iodine from the soluble product of the

reaction, the halogen is removed as far as possible by mercury and the pale yellowish-brown solution examined. As the author expected it to be a dilute solution of thiocyanogen and to behave analogously to the halogens, it was treated with (1) chlorides and bromides, whereby no appreciable effect was produced; (2) aqueous or alcoholic solutions of iodides (of cadmium, lead, silver, and mercury), whereby iodine was liberated; (3) iron powder, whereby ferric thiocyanate was produced in such quantity that the solution became opaque; (4) mercury, whereby mercurous thiocyanate was formed; (5) cuprous thiocyanate, whereby black cupric thiocyanate was formed; and (6) water, which slowly decomposed the thiocyanogen producing thiocyanic acid, hydrogen cyanide, and sulphuric acid.

The solvent ether can be replaced by acetone, absolute ethyl alcohol, chloroform, carbon tetrachloride, benzene, ethylene dibromide, or carbon disulphide. The reaction proceeds very slowly in the last solvent, but almost reaches completion in chloroform; in every case, however, a state of equilibrium appears to be attained.

The thiocyanates of potassium, zinc, cadmium, copper, and lead do not react appreciably with a solution of iodine, but mercuric thiocyanate reacts in the same way as silver thiocyanate.

Much better results are obtained with bromine. A solution of bromine in dry ethyl ether, ethyl chloride, ethyl bromide, carbon disulphide, carbon tetrachloride, chloroform, benzene, or ethylene dibromide reacts completely with the thiocyanates of silver, lead, cadmium, mercury, zinc, thallium, and copper in accordance with the equation  $2\text{MSCN} + \text{Br}_2 = 2\text{MBr} + 2\text{CNS}$ , since the resulting solution (in carbon disulphide or tetrachloride) is completely free from bromine, and in experiments with silver, lead, and mercury thiocyanates in which an excess of bromine was used, the solid product of the reaction is the pure metallic bromide. The velocity of the reaction is influenced by the solvent. A *N*-solution of bromine in carbon disulphide is decolorised by lead thiocyanate in slight excess within a few minutes, whilst about half an hour is necessary when the solvent is dry ether. A solution of bromine in carbon disulphide dried with phosphoric oxide is not decolorised by lead thiocyanate after one hour, but is almost instantly decolorised by silver or mercury thiocyanate.

The solutions of thiocyanogen obtained above are usually faintly yellow, but are occasionally quite colourless. The more concentrated solutions have a stinking odour resembling that of thiocyanic acid, and stain the skin pale red, changing to yellow. The solutions become turbid on keeping and deposit yellow or yellowish-red amorphous products. The decomposition proceeds slowly in ethyl chloride or bromide or ether, and very rapidly in carbon disulphide. The amorphous products, which are different from different solvents, appear to be mixtures consisting chiefly of polythiocyanogen,  $(\text{CNS})_x$ ; about 1% of hydrogen is also present.

Chlorine in carbon tetrachloride solution does not react with lead thiocyanate, but yields a solution of thiocyanogen and the corre-

sponding metallic chloride by shaking with an excess of silver or mercury thiocyanate; sulphur chloride and cyanogen chloride are not present in appreciable quantities in the resulting solution.

The author's usual practice for the preparation of a solution of thiocyanogen is to treat lead thiocyanate with a dry ethereal solution of bromine cooled by ice-water.

The evaporation in a vacuum over sulphuric acid of an approximately  $N/2$ -solution of thiocyanogen in ethyl chloride, bromide, or ether left a clear, viscous, unstable, yellow oil. By cooling an approximately  $N/2$ -solution in carbon disulphide to  $-70^{\circ}$ , *thiocyanogen*, CNS, is obtained in cruciform aggregates of almost colourless crystals, m. p.  $-3^{\circ}$  to  $-2^{\circ}$ . The molten substance can be supercooled to  $-20^{\circ}$ , but always resolidifies at  $-30^{\circ}$ , giving well-defined rhombic plates. By allowing it to warm to the ordinary temperature, thiocyanogen becomes reddish-brown and more viscous; finally, a yellow smoke is evolved and a dark brick red, amorphous solid is formed. Thiocyanogen dissolves extremely rapidly in ethyl alcohol or ether, but only slowly in carbon disulphide or tetrachloride. Thiocyanogen is at least as strongly electronegative as iodine.

A solution of thiocyanogen reacts with zinc and cadmium (solvent, carbon disulphide mixed with about one-fifth the volume of absolute ethyl alcohol) to form the respective thiocyanates; with mercury (solvent, carbon tetrachloride) to form mercurous thiocyanate; with aluminium (solvent, dry ether) to form an *etherate* of aluminium thiocyanate,  $\text{Al}(\text{SCN})_3 \cdot 2\text{Et}_2\text{O}$ , extremely hygroscopic, colourless plates, which become friable, and ultimately a syrup in air; with tin (solvent, carbon disulphide mixed with a small quantity of dry ether) to form an *etherate* of stannic thiocyanate,  $\text{Sn}(\text{SCN})_4 \cdot 2\text{Et}_2\text{O}$ , yellow, apparently prismatic, hygroscopic crystals, which change into a syrup in air; with arsenic (solvent, carbon disulphide) to form *arsenious thiocyanate*,  $\text{As}(\text{SCN})_3$ , almost colourless crystals; with antimony (solvent, dry ether) to form an extremely hygroscopic antimony thiocyanate (not isolated); with an excess of iron (ferrum reductum) (solvent, dry ether) to form ferrous thiocyanate, and with a deficit of iron to form anhydrous ferric thiocyanate, dark violet, crystalline powder; with manganese (solvent, ether and alcohol) to form manganous thiocyanate; with nickel (solvent, carbon tetrachloride), cobalt (solvent, carbon disulphide and alcohol), and silver (solvent, ether) to form the respective metallic thiocyanates, and with gold (solvent, none) to form, apparently, a mixture of aurous and auric thiocyanates (not isolated). Many of the experiments with metals are of a qualitative nature only.

The molecular weight of thiocyanogen cannot yet be determined. It does not yield well-defined products by treatment with organo-magnesium compounds. In order to ascertain which of its three atoms is the reactive one, a solution in dry ether was treated with mercury diphenyl, whereby phenyl thiocyanate and phenyl mercurithiocyanate,  $\text{Ph} \cdot \text{Hg}(\text{SCN})$ , m. p.  $231-232.5^{\circ}$  (Otto in 1870 gave m. p.  $226-227^{\circ}$ ), were obtained; the latter was also obtained from

phenyl mercuri-iodide and thiocyanogen in carbon disulphide solution. Etheral solutions of thiocyanogen and zinc ethyl react to form zinc thiocyanate and ethyl thiocyanate.

Thiocyanogen in solution does not yield well-defined products with ammonia or aliphatic amines, but in cold etheral solution it reacts with aniline in accordance with the equation  $2\text{PhNH}_2 + 2\text{CNS} = \text{NCS} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 + \text{PhNH}_2 \cdot \text{HSCN}$  to form aniline thiocyanate and *p*-thiocyanoaniline, colourless, odourless needles (from water), m. p. 57—57.5°. When twice the quantity of thiocyanogen is used, the product is *p*-thiocyanoaniline thiocyanate, faintly red crystals. By reduction with hydrochloric acid and zinc dust, *p*-thiocyanoaniline yields *p*-aminophenyl mercaptan, which was identified by oxidation to the corresponding disulphide. In a similar manner, thiocyanogen and dimethylaniline react in etheral solution to form dimethylaniline thiocyanate and *p*-thiocyanodimethylaniline,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SCN}$ , colourless, odourless crystals, m. p. 73—74°, which yields *p*-dimethylaminophenyl mercaptan by reduction. Diphenylamine and thiocyanogen in etheral solution yield thiocyanic acid and ? : ?-dithiocyanodiphenylamine,  $\text{NH}(\text{C}_6\text{H}_4 \cdot \text{SCN})_2$ , faintly greenish-yellow needles, m. p. 120°, whilst triphenylamine under similar conditions yields thiocyanic acid and ? : ?-dithiocyanotriphenylamine, needles, m. p. 115—116°.

Phenol and thiocyanogen in carbon disulphide solution react to form thiocyanic acid (which was not detected, however, being apparently converted by a secondary reaction into an insoluble, yellowish-brown substance) and *p*-thiocyanophenol, colourless, odourless plates of rhombic habit, m. p. 53—54°, the constitution of which was proved by its conversion through *p*-hydroxyphenyl mercaptan into *pp'*-dihydroxydiphenyl disulphide, and also by its formation from *p*-thiocyanoaniline by the diazo-reaction.

Some experiments on the competition of iodine and thiocyanogen in solution for a metal show that the equilibrium  $\text{MSCN} + \text{I} \rightleftharpoons \text{MI} + \text{CNS}$  is largely dependent on the nature of the metal; in the case of cadmium, the reaction from right to left is practically irreversible.

Stannous thiocyanate, produced by the interaction of lead thiocyanate and stannous sulphate in aqueous solution, and obtained in colourless crystals from the hot filtrate after removing lead sulphate, is converted into the etherate of stannic thiocyanate by a solution of thiocyanogen in a mixture of carbon disulphide and ether.

An etheral solution of thiocyanogen reacts with mercuric cyanide (and also with silver or zinc cyanide) to form mercuric thiocyanate and a substance which is identical with the cyanogen sulphide,  $(\text{CN})_2\text{S}$ , described by Linnemann and by Schneider; from this method of preparation, the substance might be cyanogen thiocyanate,  $\text{CN} \cdot \text{SCN}$ .

Several investigators have recorded the production of a very unstable, blood-red substance when a concentrated aqueous solution of potassium thiocyanate is acidified with sulphuric acid and treated

with a solution of sodium nitrite. This substance, which almost immediately decomposes, with the evolution of nitric oxide, can also be obtained by treating a solution of nitrosyl chloride in carbon tetrachloride with silver thiocyanate at the ordinary temperature. It appears to be *nitrosyl thiocyanate*,  $\text{NO}\cdot\text{SCN}$ , since its solution, which is relatively stable at  $-17^\circ$ , converts cuprous thiocyanate into cupric thiocyanate and metallic mercury into mercurous thiocyanate, and reacts with aqueous sodium hydroxide to form sodium thiocyanate and sodium nitrite. The author has performed some preliminary experiments in which the substance is produced from nitric oxide and thiocyanogen in well-cooled carbon disulphide. The substance allies itself with the nitrosyl haloids in its properties, its position falling between those of the bromide and iodide.

Although its molecular weight cannot yet be ascertained, the author is of opinion that the molecular magnitude and the constitution of thiocyanogen in solution are represented by the formula  $\text{CN}\cdot\text{S}\cdot\text{S}\cdot\text{CN}$ . In accordance with this nitrile structure, a dry ethereal solution of thiocyanogen reacts with dry ethereal hydrogen chloride cooled with ice-water to form a precipitate of a colourless, crystalline *substance*,  $2\text{CNS}, 2\text{HCl}$  (which becomes yellow above  $100^\circ$  and changes gradually to a brown substance without melting), and a solution of a *substance*,  $2\text{CNS}, \text{HCl}$ , pale yellow prisms or plates of rhombic habit, m. p.  $69-70^\circ$ . In contrast to the former, the latter substance, which is not formed when carbon disulphide, carbon tetrachloride, chloroform, or benzene is employed as solvent, is easily soluble in organic solvents and is unaffected by hot water. The substance,  $2\text{CNS}, 2\text{HCl}$ , is converted by water into a *substance*, pale yellow, rhombic leaflets or needles, which decomposes without melting when heated, and has the composition of thiocyanogen hydrate,  $(\text{CNS})_2, \text{H}_2\text{O}$ . The latter substance is regarded as 2-imino-5-keto-1:3:4-dithioazolidine,  $\text{NH} < \begin{array}{c} \text{CO} \text{---} \text{S} \\ \text{C}(\text{:NH}) \end{array}$ , since it presents

several points of analogy to perthiocyanic acid (2-imino-5-thio-1:3:4-dithioazolidine; Hantzsch and Wolvekamp, A., 1904, i, 718), particularly in its behaviour with cold aqueous potassium hydroxide, whereby sulphur is liberated and a colourless, crystalline *substance*,  $\text{C}_2\text{ON}_2\text{SK}_2$  (*potassium cyanoiminothiocarbonate*,  $\text{CN}\cdot\text{N}:\text{C}[\text{SK}]\cdot\text{OK}$ ),

analogous to potassium dithiocyanate (cyanoiminodithiocarbonate), produced. The substance  $2\text{CNS}, 2\text{HCl}$  is probably 5:5-dichloro-2-imino-1:3:4-dithioazolidine,  $\text{NH} < \begin{array}{c} \text{CCl}_2 \text{---} \text{S} \\ \text{C}(\text{:NH}) \end{array}$ . When suspended in benzene, it reacts with aniline to form the hydrated hydrochloride of Fromm's thiuret (A., 1893, i, 575),  $\text{C}_6\text{H}_7\text{N}_3\text{S}_2, \text{HCl}, 3\text{H}_2\text{O}$ .

C. S

### Photochemical Oxidation of Potassium Thiocyanate.

DOMENICO GANASSINI (*Boll. Chim. Farm.*, 1919, **58**, 457-463).—Under the influence of sunlight, aqueous potassium thiocyanate solutions undergo change, in which the atmospheric oxygen takes



part. With solutions of medium concentration, this change takes place with great rapidity, an amorphous, yellow precipitate of pseudocyanogen sulphide separating in most cases; if the concentration is either above or below a certain limiting value, the change is either entirely prevented or proceeds only very slowly. The concentration of the thiocyanate most favourable to the separation of pseudocyanogen sulphide is about 50% in the summer and about 10% in the winter. The purer potassium thiocyanates, especially those quite free from traces of ferrous salts, are more sensitive to this reaction than less pure preparations.

In addition to pseudocyanogen sulphide, the photochemical decomposition of potassium thiocyanate yields as constant products hydrocyanic and sulphuric acids, carbon dioxide, and ammonium salts,  $12\text{KCNS} + 12\text{O}_2 + 6\text{H}_2\text{O} = 6\text{K}_2\text{SO}_4 + 3\text{HCN} + 3\text{CO}_2 + 3\text{NH}_3 + 2(\text{CNS})_3$ . Further, there is always formed an unstable, intermediate peroxygenated compound, which imparts a blue colour to fresh guaiacum tincture, and is possibly analogous to Caro's acid.

Normal, decinormal, and centinormal solutions of potassium thiocyanate undergo these alterations, but only with the first of these does separation of pseudocyanogen sulphide take place. Although decomposed in this way, the deci- and centi-normal solutions show, within certain limits of time, no sensible diminution in titre, probably owing to the replacement, at least in the early stages of the change, of the thiocyanate by an equivalent proportion of the cyanide.

T. H. P.

**Direct Passage from the Nitrous Esters and Nitro-compounds to Nitriles by Catalysis.** ALPH. MAILHE and (MME) M. L. BELLEGARDE (*Bull. Soc. chim.*, 1919, [iv], 25, 588—593).—By the catalytic hydrogenation of *isoamyl* nitrite by means of reduced nickel at  $280^\circ$ , primary, secondary, and tertiary amines result, with a small amount of *isovaleronitrile*. If the temperature of hydrogenation is increased to  $300$ — $320^\circ$ , the yield of nitrile is considerably increased at the expense of the amines. At the same time, a certain amount of *isoamyl* alcohol is obtained, owing to hydrolysis of some of the nitrite, and a portion of the alcohol then undergoes dehydrogenation, giving the corresponding aldehyde. Similar results were obtained with propyl, *isobutyl*, and heptyl nitrites.

In the same way, at temperatures above  $300^\circ$ , nitromethane gave some hydrogen cyanide and nitropentane some *isovaleronitrile*.

W. G.

**Fixation of Nitrogen in the Form of Hydrogen Cyanide by means of an Electric Arc.** E. BRINER and A. BAERFUSS (*Helv. Chim. Acta*, 1919, 2, 663—666).—Mixtures of hydrocarbons and nitrogen when submitted to the action of an electric arc produce hydrogen cyanide in yields much superior to the yield of ammonia obtained from nitrogen and hydrogen. The method employed is similar to that previously described (A., 1919, ii, 338).

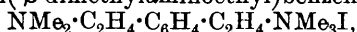
The mixture of gases circulates at the rate of 8—10 litres per hour in a chamber where an arc of 0.020 amp. is burning between platinum electrodes 7 mm. apart. Using 12 parts of methane, 23 of nitrogen, and 65 of hydrogen under 635 mm. pressure, 0.08% by volume of hydrogen cyanide is obtained. This gives a yield of 0.46 gram of hydrogen cyanide per kilowatt hour, in addition to a yield of 0.14 gram of ammonia per kilowatt hour. In this case, the *E.M.F.* applied was 1020 volts. With the same mixture, but with an *E.M.F.* of 420 volts, 0.12% by volume of hydrogen cyanide was obtained, which is 1.75 gram per *K.W.H.* and 0.44 gram of ammonia per *K.W.H.* The best case examined is with a mixture of 1 part of methane and 5 of nitrogen at 505 volts, where a yield of 0.75% by volume of hydrogen cyanide was obtained, which is 7.39 grams of hydrogen cyanide per *K.W.H.* and 0.48 gram of ammonia per *K.W.H.*

J. F. S.

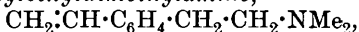
**Action of Carbon Monoxide on Sodium Alkyls.** WALTER SCHOELLER, WALTER SCHRAUTH, and WALTER ESSERS (*Ber.*, 1920, **53**, [B], 62—63).—In reference to Schlubach's communication on this subject (this vol., i, 19), reference is given to earlier work by the authors on the action of carbon monoxide on mercury acetate (*A.*, 1913, i, 1162).

J. C. W.

**Preparation of *o*-Divinylbenzene.** JULIUS VON BRAUN and LUDWIG NEUMANN (*Ber.*, 1920, **53**, [B], 109—113).—The pure methiodide of *o*-di-( $\beta$ -dimethylaminoethyl)benzene,



has m. p. 196°, and not 175—185° as previously stated (*A.*, 1917, i, 130). When boiled with sodium hydroxide in a current of steam, the salt is decomposed into an amorphous, pale yellow *polymeride* of *o*-divinylbenzene,  $\text{C}_6\text{H}_4(\text{CH}:\text{CH}_2)_2$ , m. p. 206—207°, and also  $\beta$ -*o*-vinylphenylethyldimethylamine,



which passes over in the steam. The base has b. p. 123—124°/13 mm., and forms a *picrate*, yellow leaflets, m. p. 137°, a *platinochloride*, m. p. 167°, and a silvery *methiodide*, m. p. 209°. The corresponding quaternary ammonium hydroxide is stable in solution, but yields the above polymeride on evaporation. Seeing that the isolated unsaturated base is so stable, it appears that the extensive decomposition which it suffers in the above reaction is "induced" by the decomposition of the other group. J. C. W.

**The Two Isomeric Diphenylindenes.** A. ORÉKHOFF (*Bull. Soc. chim.*, 1919, [iv], **25**, 598—600).—The author shows that the diphenylindene obtained by him by the action of heat on  $\alpha\beta\gamma$ -triphenylpropene dibromide (compare *A.*, 1914, i, 265) is really the  $\alpha\beta$ -diphenylpropene, and that during the formation of its benzylidene derivative or its oximino-derivative it undergoes isomerisation to the  $\beta\gamma$ -diphenylindene described by Thiele and Ruggli (compare *A.*, 1912, i, 866).

W. G.

**Action of Light on 1-10-Bromophenanthrene-3(or 6)-sulphonic Acid.** HÅKAN SANDQVIST (*Arkiv Kem. Min. Geol.*, 1917-18, 7, No. 4, 1-14).—In a previous paper (A., 1915, i, 795), the author has shown that the action of light on aqueous solutions of 10-bromophenanthrene-3(or 6)-sulphonic acid in hydrochloric acid decreases the viscosity of the solution, and has explained this as being due to the light changing an *a*-form of the acid into the *b*-form. Each form was supposed to give salts with different solubilities, water of crystallisation, etc., but the further experiments of the author with the barium salt have not led to the isolation of two such isomerides. However, from the more soluble fractions of the barium salt, which had been exposed to an intense light, a reddish-brown to black, varnish-like acid was obtained, which immediately lowered the viscosity of a sulphonic acid-hydrochloric acid mixture when added to it. From this dark acid, the dimethyl ester was prepared, and analysis showed it to be *dimethyl monobromodiphenanthryldisulphonate* (annexed formula); the *barium* salt was

$$\begin{array}{l} \text{(?) } C_{14}H_7 \begin{array}{l} \swarrow \text{Br} \\ \searrow \text{SO}_3\text{Me} \end{array} \text{ (3 or 6)} \\ | \\ \text{(10')} C_{14}H_8 - \text{SO}_3\text{Me} \text{ (3' or 6')} \end{array}$$

$C_{28}H_{18}Br(SO_3)_2Ba$ . It is the production of this acid by the action of light (oxidation) on the original sulphonic acid which causes the decrease in viscosity; the addition of 0.02% to the sulphonic acid-hydrochloric acid solution lowers the viscosity to one-third of its former value.

From the mother liquors of the above-mentioned barium salt another substance was isolated, but not identified, which lowered the viscosity, but not to such a great extent. Phenanthraquinone-3-sulphonic acid exerts a still less effect. The product formed, together with 11-10-bromophenanthrene-3(or 6)-sulphonic acid in the bromination of phenanthrene-3-sulphonic acid (*ibid.*, 1917, 6, No. 13, 13) has exactly the same effect as the above-mentioned product of the action of light, and is therefore probably the same substance.

It is shown experimentally that the presence of monobromodiphenanthryldisulphonic acid or its barium salt accounts for the differences in solubility, etc., described in the previous paper (*loc. cit.*).

T. S. P.

**Amine Oxidation. I. Oxidation of Aniline.** STEFAN GOLDSCHMIDT (*Ber.*, 1920, 53, [B], 28-44).—In Bamberger's interpretation of the oxidation of aniline, phenylhydroxylamine is regarded as the initial product. Whilst this compound may very well lead ultimately to nitrobenzene, it does not offer a satisfactory explanation of the formation of the polynuclear oxidation products, since it is not sufficiently reactive. It has been shown, however, that benzoquinonephenyldi-imine, which is regarded as the precursor of aniline-black, and azobenzene, are the first demonstrable products of the oxidation by alkaline permanganate or bleaching powder, whereas these are not formed under conditions appropriate to the production of phenylhydroxylamine, and ultimately nitro-

benzene. It appears, therefore, that there are two different initial products, varying according to the conditions. Agents which readily yield atomic oxygen, such as Caro's acid or hydrogen peroxide, produce aniline oxide, and further developments follow as in the scheme:  $\text{PhNH}_2 \rightarrow \text{PhNH}_2\text{:O} \rightarrow \text{PhNH}\cdot\text{OH} \rightarrow \text{PhNO} \rightarrow \text{PhNO}_2$ , and  $\text{PhNO} + \text{PhNH}\cdot\text{OH} \rightarrow \text{PhN}-\text{NPh}$ , and



$\text{PhNO} + \text{PhNH}_2 = \text{PhN}:\text{NPh}$ . Under other conditions, however, the initial stage is represented by the removal of two atoms of hydrogen, subsequent changes being due to the activity of the  $\text{PhN}:$  residue (compare A., 1913, i, 1173). This radicle may, for example, polymerise to azobenzene, benzoquinonephenyldi-imine,  $\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{NH}$ , or emeraldine. This assumption is based on the fact that azo-compounds and quinonearyldi-imines can be isolated when aniline, and especially its nuclear-substituted methyl homologues having free para-positions, are oxidised by lead peroxide. The theory is considerably strengthened by the further fact that mixed azo-compounds and mixed quinonearyldi-imines are produced when two amines are oxidised together.

The methylated quinonearyldi-imines are easily hydrolysed by acids to the original amine and the quinone, and may thus be identified. They differ, therefore, from unsubstituted benzoquinonephenyldi-imine, which mainly polymerises to emeraldine. This explains, therefore, why Willstätter obtained only duroquinone in an attempt to oxidise aminodurene in acid solution to a methylated emeraldine (A., 1909, i, 899).

In the oxidation of aniline itself, the base is dissolved in ether and shaken with lead peroxide and anhydrous sodium sulphate. The filtered oxidation products are then shaken with alcohol, ammonium chloride, and zinc dust to reduce the benzoquinonephenyldi-imine to *p*-aminodiphenylamine. A current of steam removes unchanged aniline and azobenzene, whilst the diamine is isolated as the sulphate. In the other cases, the ethereal solution is oxidised by lead peroxide and glacial acetic acid, the di-imine is then reduced by zinc dust, and the colourless solution is shaken with sodium carbonate to remove acetic acid. The dry ethereal solution is finally mixed with alcoholic oxalic acid to precipitate the oxalate of the aminodiarylamine.

*Aminodidurylamine*,  $\text{C}_{20}\text{H}_{28}\text{N}_2$ , crystallises in concentric groups of needles, m. p.  $157^\circ$ , and may be oxidised by lead peroxide to *duroquinoneduryldi-imine*,  $\text{C}_6\text{HMe}_4\cdot\text{N}:\text{C}_6\text{Me}_4\cdot\text{NH}$ , druses of reddish-brown needles, m. p.  $155\text{--}156^\circ$ , which yields aminodurene and *p*-duroquinone, m. p.  $110^\circ$ , when mixed with an excess of hydrochloric acid.

1-Amino-2:3:5-cumene gives rise to *azocumene* [2:3:5:2':3':5'-hexamethylazobenzene], m. p.  $152\text{--}153^\circ$ , *aminodicumylamine*,  $\text{C}_{18}\text{H}_{24}\text{N}_2$ , m. p.  $138\text{--}139^\circ$ , and *cumoquinonecumyldi-imine*,  $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{N}:\text{C}_6\text{HMe}_3\cdot\text{NH}$ , stout prisms, m. p.  $103^\circ$ .

From *m*-4-xylidine are prepared azoxylene (2:3:2':3'-tetramethylazobenzene), m. p.  $111^\circ$ , *aminodixylamine* [4-amino-

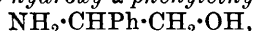
2:3:2':3'-tetramethyldiphenylamine], m. p. 74—75°, and *xyloquinonexylyldi-imine*, brown rosettes, m. p. 67.5—68.5°.

The oxidation of a mixture of aminodurene and *m*-4-xylidine is described. The isolation of the products presents some difficulties, but *xylylamino-durylamine* [4-amino-2:3:5:6:2':3'-hexamethyldiphenylamine], m. p. 153—154°, is certainly identified by its oxidation to *duroquinonexylyldi-imine*, m. p. 83—84°, and hydrolysis of this to duroquinone and the xylidine. *Azodurene* is also present; it forms reddish-yellow tablets, m. p. 80—81°. J. C. W.

**Intramolecular Rearrangement of the Alkylarylamines: Formation of 4-Amino-*n*-butylbenzene.** JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM (T., 1920, 117, 103—137).

**New Method for the Preparation of Alkylamines.** JIRO TAKEDA and SAJURO KURODA (*J. Pharm. Japan*, 1919, 449, 561—608).—Styrene dibromide and carbamide react at 120—130°

to form 2-amino-4-phenyl-4:5-dihydro-oxazole,  $\text{O} \begin{array}{c} \text{CH}_2 \text{---} \text{CHPh} \\ \diagup \quad \diagdown \\ \text{C}(\text{NH}_2) \text{:N} \end{array}$ , the hydrolysis of which by alcoholic potassium hydroxide at 150° yields ammonia and  $\beta$ -hydroxy- $\alpha$ -phenylethylamine,

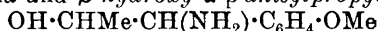


the *dibenzoyl* derivative, m. p. 155°, of which has also been prepared by the following series of reactions, which prove its constitution:  $\text{COPh} \cdot \text{CH}_2 \text{Br} \rightarrow \text{COPh} \cdot \text{CH}_2 \cdot \text{OAc} \rightarrow \text{COPh} \cdot \text{CH}_2 \cdot \text{OH} \rightarrow \text{NOH} \cdot \text{CPh} \cdot \text{CH}_2 \cdot \text{OH} \rightarrow \text{NH}_2 \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{OH} \rightarrow \cdot$



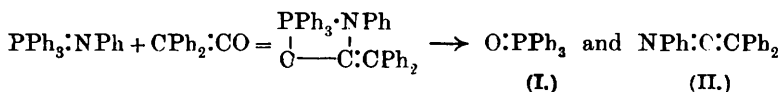
On the assumption that the reactions proceed analogously to the preceding, anethole dibromide heated with half its weight of carbamide at 120—130° yields 2-amino-4-*p*-anisyl-5-methyl-4:5-dihydro-oxazole,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{array}{c} \text{N} = \text{C} \cdot \text{NH}_2 \\ \diagup \quad \diagdown \\ \text{CHMe} \cdot \text{O} \end{array}$ , rectangular columns, m. p.

165°, the hydrolysis of which by alcoholic potassium hydroxide produces ammonia and  $\beta$ -hydroxy- $\alpha$ -*p*-anisylpropylamine,

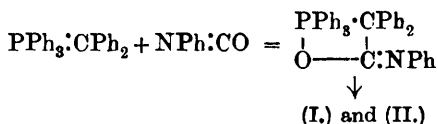


(hydrochloride, m. p. 193°; copper derivative, m. p. 113°). Bromoanethole dibromide and isosafrole dibromide also react with carbamide, yielding corresponding oxazolines, m. p. 20° and 175° respectively. CHEMICAL ABSTRACTS.

**Ketens. XXX. Preparation of a Keten-imine Derivative from Diphenylketen.** H. STAUDINGER and JULES MEYER (*Ber.*, 1920, 53, [B], 72—76).—Triphenylphosphinephenylimine (this vol., i, 107) reacts with diphenylketen in benzene solution in an atmosphere of nitrogen to form triphenylphosphine oxide (I) and diphenylketenphenylimine (II), thus:



The same products are formed when triphenylphosphinediphenylmethyle (ibid., 106) is treated with phenylcarbimide, thus:



In either case, the oxide is precipitated by the addition of light petroleum.

*Diphenylketenphenylimine* crystallises in transparent, pale yellow tablets, m. p. 55—56°, b. p. 190—195°/abs. vac. It has been sought for some time, in order to compare its properties with those of compounds with other systems of twin double linkings, such as ketens,  $\text{—C:C:O}$ , and carbimides,  $\text{—N:C:O}$ . Quite unexpectedly, the new compound, with the system  $\text{—N:C:C—}$ , is very stable and resistant to air, water, alcohol, and bases. When warmed with concentrated hydrochloric acid, however, it yields diphenylacetanilide.

J. C. W.

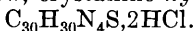
### Certain Completely Substituted Aromatic Iminosulphides.

H. RIVIER and CH. SCHNEIDER (*Helv. Chim. Acta*, 1920, 3, 115—134).—The authors give an extended review of the literature relating to the formation of substances containing the group  $\text{C—S—C—N}$ , and their isomerides with the group  $\text{C—N—C—S}$ . The possibility of assigning definite formulæ to the substances is based on the fact that the chromophore,  $\text{C=S}$ , is much more active than the group,  $\text{C—S—C}$ . From this point of view, the authors have revised and extended the work of Jamieson (A., 1904, i, 396), and have prepared a series of compounds which are either yellow or red, and which are therefore held to contain the groups  $\text{—C—S—C—}$  and  $\text{C=S}$  respectively. In only one case has the direct conversion of one form into the other proved possible, but a general consideration of the constitution of the products which have been isolated appears to justify the conclusion that stability is conditioned by symmetry of the molecule. It is, however, remarkable that in the sole instance of actual transformability, conversion is from the symmetrical to the less symmetrical form.

Benzanilide sulphide,  $\text{NPh:CPh·S·CPh:NPh}$ , intensely yellow prisms, m. p. 211—212° (Jamieson, *loc. cit.*; Raffo and Rossi, A., 1915, i, 86, give 202—204°), is most conveniently prepared by the action of benzanilideiminochloride on the potassium salt of thio-benzanilide. It is converted by hydrogen chloride in ethereal solution into the corresponding *chloride*, an amorphous, red mass, which is decomposed on exposure to moist air.

$\alpha$ -Thiobenznapthalide, yellow crystals, m. p. 149—150°, and  $\beta$ -thiobenznapthalide, yellow leaflets, m. p. 160—162°, are prepared by the action of phosphorus pentasulphide on a solution of the corresponding benznaphthalides in solvent naphtha.  $\alpha$ -Benznapthalide sulphide,  $\text{S(CPh·N·C}_{10}\text{H}_7)_2$ , yellow, crystalline powder, m. p. 130—131°, is formed in the same manner as benzanilide

sulphide; when its solutions are boiled for some time or are evaporated, it becomes transformed into *thiobenzoyldi- $\alpha$ -naphthylbenzenylamidine*,  $C_{10}H_7 \cdot N : CPh \cdot N(C_{10}H_7) \cdot CPh : S$ , red crystals, m. p. 156—157°, but the reverse change could not be effected. Hydrogen chloride and concentrated sulphuric acid convert the yellow substance into red salts, which are decomposed by excess of acid, whilst the red material is decomposed by acid, with formation of benznaphthalide and thiobenznaphthalide. The action of benzanilide iminochloride on potassium  $\alpha$ -thiobenznaphthalide or of  $\alpha$ -benznaphthalide iminochloride on potassium thiobenzanilide yields the substance,  $NPh : CPh : S \cdot CPh : N \cdot C_{10}H_7$ , yellow crystals, m. p. 176—177°, which yields an unstable, red *hydrochloride*, which is decomposed by excess of acid into thiobenzanilide and  $\alpha$ -benznaphthalide, showing that in the transformation which precedes the decomposition, it is the group  $NPh$ , and not  $N \cdot C_{10}H_7$ , which has exchanged places with the sulphur atom. Attempts to prepare  $\beta$ -benznaphthalide sulphide or the sulphide of benzanilide and  $\beta$ -benznaphthalide were unsuccessful. *p*-*Dimethylaminobenzanilide sulphide*,  $S[C(C_6H_4 \cdot NMe_2) : NPh]_2$ , yellow needles or prisms, m. p. 155—156°, is best prepared by the action of potassium sulphide on *p*-dimethylaminobenzanilideiminochloride hydrochloride; it yields a yellow, crystalline *hydrochloride*,



Excess of hydrochloric or sulphuric acid does not decompose the salts, which thus appear to have the same constitution as the free base.

The action of thiobenzoyl chloride,  $Ph \cdot CSCl$ , on diphenylbenzenylamidine, on *di- $\alpha$ -naphthylbenzenylamidine*, pale yellow leaflets, m. p. 160—161°, and on *di- $\beta$ -naphthylbenzenylamidine*, colourless crystals, m. p. 154—155°, has been investigated; in the first case, benzanilide sulphide was obtained, whilst positive results were not given by the naphthalene derivatives.

Benzoylthiobenzanilide,  $COPh \cdot NPh \cdot CSPh$ , red prisms, m. p. 108—109° (compare Jamieson, *loc. cit.*), *benzoyl- $\alpha$ -thiobenznaphthalide*, red crystals, m. p. 145—146°, and *benzoyl- $\beta$ -thiobenznaphthalide*, red crystals, m. p. 129—130°, were prepared by the gradual addition of a solution of benzoyl chloride in chloroform to the requisite thioanilide or thiobenznaphthalide dissolved in the calculated quantity of alcoholic potassium hydroxide. They are decomposed by hydrogen chloride in ethereal solution, even if only one molecular proportion of the acid is used, yielding benzoyl chloride and the corresponding thioanilide. They are soluble in concentrated sulphuric acid without decomposition, but addition of water precipitates the thioanilide.

H. W.

**[Preparation of] Phenolic Compounds.** E. H. ZOLLINGER and H. ROEHLING (U.S. Pat. 1321271).—Lead compounds which form insoluble or sparingly soluble compounds with phenols are made to react with aromatic halogen compounds and a hydroxide of an alkali or alkaline earth metal. The reaction is facilitated by

catalysts, such as copper or copper compounds, iodides of alkali or alkaline earth metals, iodates, vanadium, titanium, molybdenum, and rare earths and their salts. Thus *o*-chlorophenol is heated for about forty-five minutes at 250° with an aqueous solution of lead acetate and sodium hydroxide (alternatively, lead sulphate or hydroxide at 260° with copper iodide as catalyst), whereby the lead salt of catechol is formed, which crystallises on cooling.

Among the examples recorded is the formation of cresolsulphonic acid from chloro- or bromo-toluenesulphonic acids, orcinol from bromocresol or dibromotoluene, catechol-4-sulphonic acid from sodium 1:2-dichlorobenzene-4-sulphonate, 3:5-dihydroxybenzoic acid from 3:5-dihalogenobenzoic acids, salicylaldehyde from *o*-chlorobenzaldehyde,  $\alpha$ - and  $\beta$ -naphthols from the respective chloro-naphthalenes, and alizarin from 1:2-dichloroanthraquinone.

CHEMICAL ABSTRACTS.

**The Preparation of 2:4-Dinitrophenetole and 2:4:6-Trinitrophenetole.** M. MARQUEYROL and SCOHY (*Bull. Soc. chim.*, 1920, [iv], 27, 105—107).—2:4-Dinitrophenetole may readily be prepared by the action of aqueous sodium hydroxide on an alcoholic solution of 1-chloro-2:4-dinitrobenzene at 36°, gradually rising to 55°. If this phenetole is then nitrated in sulphuric acid solution at 30—40°, an excellent yield of 2:4:6-trinitrophenetole is obtained.

W. G.

**The Synthesis of Aldehydes and Hydroxy-acids by means of Secondary *aaa*-Trichloro-alcohols.** PIERRE HÉBERT (*Bull. Soc. chim.*, 1920, [iv], 27, 45—55).—Bossneck's method for the preparation of aldehydes or hydroxy-acids by the action of potassium hydroxide on *aaa*-trichloro-secondary alcohols (compare A., 1885, 976; 1886, 458) is shown to be generally applicable in the aliphatic, cyclic, aromatic, naphthalene, and aryl aliphatic series. The potassium hydroxide may be replaced by the hydroxides of sodium, calcium, magnesium, or barium, or advantageously by sodium carbonate. The trichloro-alcohols of the aliphatic series do not give such good yields as do the aromatic alcohols, where the  $\cdot\text{CH}(\text{OH})\cdot$  group is directly attached to a ring carbon atom. The activity in the aromatic series is diminished if this group is separated from the nucleus by one or more carbon atoms. The following new compounds are described.

By condensing magnesium *p*-bromophenyl bromide with anhydrous chloral,  $\beta$ -*p*-bromophenyltrichloromethylcarbinol,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{CH}(\text{OH})\cdot\text{CCl}_3$ ,

b. p. 183—187°/18 mm., is obtained, giving an *acetate*, m. p. 145—147°, and this on decomposition with sodium carbonate gives *p*-bromobenzaldehyde and *p*-bromophenylglycollic acid.

Magnesium benzyl bromide reacts with chloral to give *phenyl-trichloroisopropyl alcohol*,  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{OH})\cdot\text{CCl}_3$ , b. p. 158—160°/18 mm., giving an *acetate*, m. p. 110—111°.

*o*-4-Xylyltrichloromethylcarbinol is decomposed by sodium



carbonate, giving 3:4-dimethylbenzaldehyde and 3:4-dimethyl-phenylglycollic acid,  $C_6H_3Me_2 \cdot CH(OH) \cdot CO_2H$ , m. p. 115—116°.

Ethyl  $\alpha$ -naphthylglycollate,  $C_{10}H_7 \cdot CH(OH) \cdot CO_2Et$ , has m. p. 68—69°.

W. G.

**Mercury Benzoate.** ROBERT WOOD TERRY (*Midl. Drug. and Pharm. Rev.*, 1919, **53**, 222—225; from *Chem. Zentr.*, 1919, iii, 866).—A 1% solution of mercury benzoate is obtained by dissolving 2.715 parts of mercuric chloride and 2.880 parts of sodium benzoate in 442 parts of water, and filtering after a week.

H. W.

**Abietic Acid.** DAVID JOHANSSON (*Arkiv Kem. Min. Geol.*, 1917, **6**, No. 19).—Very little is known as to the derivatives and decomposition products of abietic acid. The author has therefore sought evidence of its unsaturation and of the presence in its molecule of the aromatic and hydroaromatic nuclei postulated by previous investigators (compare Easterfield and Bagley, T., 1904, 1238; Levy, A., 1913, i, 620). The acid, prepared from American colophony by Hunt and Pochin's process, had m. p. 168—173° (sintering at 155°), and in alcoholic solution  $[\alpha]_D^{20} - 28.6^\circ$ . Both the Hübl-Waller and the Winkler iodine numbers increased with the duration of the determination, respective values of 102—171 and 150—357 being obtained. Since, approximately, the same values were obtained from the dihydro-derivative (below), and this behaviour was reproduced by the congener *d*-pimaric acid and its dihydro-derivative, it would appear that the unreduced acids contain at least two double bonds, which are not equivalent, or that substitution takes place. Halogenated compounds could not, however, be isolated. Dihydroabietic acid,  $C_{20}H_{32}O_2$ , m. p. 173—178° (sintering at 156°), was obtained by hydrogenation in ethereal solution in presence of platinum-black. Unlike abietic acid, it is unchanged after long exposure. Treated with chloroform and glacial acetic and sulphuric acids, it gives a reddish-violet colour, changing to yellowish-brown, whilst abietic acid gives a deep blue colour, which becomes brownish-green. From sulphonation experiments, a very small proportion of a mixture of acids was obtained. Dinitroabietic acid,  $C_{20}H_{28}O_2(NO_2)_2$ , produced by nitration with fuming acid below 10°, separates from acetone in needles, m. p. 178—184°,  $[\alpha]_D^{20} + 44.26^\circ$ , which, on exposure to sunlight, turn red in a few seconds, and eventually brownish-green. The sodium salt,  $C_{20}H_{27}O_2(NO_2)_2Na \cdot 1\frac{1}{2}H_2O$ , needles, the potassium salt, and the barium salt,  $[C_{20}H_{27}O_2(NO_2)_2]_2Ba \cdot 4H_2O$ , yellowish-white needles, crystallise much better than those of abietic acid; the silver salt,  $C_{20}H_{27}O_2(NO_2)_2Ag$ , is a flocculent precipitate. In contrast with abietic acid, its dinitro-derivative is esterified by treatment with alcohol and hydrochloric acid. The methyl ester forms needles, m. p. 178—182°. The ethyl ester,



needles, m. p. 156—158°, is best prepared from the silver salt, and

is only hydrolysed by alkali with difficulty. Molecular compounds of the dinitro-derivative with, in some cases, four, and in others six, molecular proportions of naphthalene, anthracene, phenanthrene, and retene separate from alcohol in white needles, stable to light, which respectively melt at 110—117° (decomp.), 244—246°, 235—236°, and 234—238°. *Diamino-abietic acid dihydrochloride*,  $C_{20}H_{28}O_2(NH_2, HCl)_2$ , is a brown, amorphous powder, m. p. 280°, and very hygroscopic. A tarry product was obtained in an attempt to remove the amino-group by diazotisation. Crystallographic data are given for abietic, dihydroabietic, and dihydro-dextropimaric acids. The presence of an aromatic or hydroaromatic nucleus in the molecule of abietic acid is regarded as now definitely determined. J. K.

**The Action of Nitrites on some Imino-ethers.** A. BERTON (*Arkiv Kem. Min. Geol.*, 1918—1919, 7, No. 13, 1—21).—The product of the action of nitrous acid on ethyl benzoyliminoacetate is not a nitroso-derivative (Haller, A., 1887, 826), but is identical with ethyl oximinobenzoylacetate (Perkin, T., 1885, 47, 243). *Ethyl imino-oximinobenzoylacetate*,  $COPh \cdot C(NO) \cdot C(NH) \cdot OEt$ , leaflets, m. p. 112°, is obtained as the intermediate product when a cold solution of ethyl iminobenzoylacetate is added to a cold solution of sodium nitrite, and passes into ethyl oximinobenzoylacetate on warming or when treated with acids. Further, chloro-oximinoacetophenone, by treatment with potassium cyanide and hydrochloric acid, furnishes oximinobenzoylacetoneitrile (E. v. Meyer, A., 1885, 582), which is converted by hydrochloric acid in alcoholic solution into the hydrochloride of ethyl imino-oximinobenzoylacetate. The *hydrochloride*,  $C_{11}H_{13}O_3N_2Cl$ , m. p. 114°, is precipitated by leading dry hydrogen chloride into its ethereal solution. It can also be similarly obtained from the product of the action of amyl nitrite on an ethereal solution of ethyl iminobenzoylacetate, whilst, by passing dry ammonia into a similar solution or a solution of ethyl imino-oximinobenzoylacetate in alcohol, *oximino-benzoylacetamidine*,  $C_9H_9O_2N_3$ , sulphur-yellow crystals, m. p. 227—229°, is produced. Its *hydrochloride*,  $C_9H_{10}O_2N_3Cl$ , is faintly yellow, and begins to lose hydrochloric acid at 200°. The *sulphate*,  $C_9H_{11}O_5N_3S$ , melts at 195°.

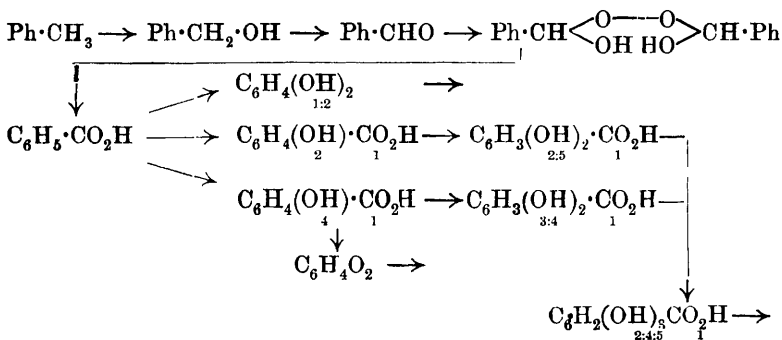
The action of nitrous acid on ethyl iminophenylacetate leads to the formation of ethyl phenylacetate and phenylacetamidine nitrite,  $CH_2Ph \cdot C(NH) \cdot NH_2 \cdot HNO_2$  (Lossen, *Diss.*, Koenigsberg, 1890; Kammer, *ibid.*, 1893), m. p. 147°. This compound was further identified by the preparation of its acetate, m. p. 195°, and its nitrate, m. p. 166—167°, and its conversion into phenylacetamide by the action of sodium hydroxide.

In agreement with Knorr's view (A., 1917, i, 255) that the formation of amidines by the action of ammonia on the hydrochlorides of imino-esters is conditioned by ammonium chloride, it is shown that the nitrate of *p*-tolylacetamidine is produced by the action of ammonium nitrate on ethyl imino-*p*-tolylacetate. J. K.

**Electrochemical Oxidation of Benzaldehyde and Benzoic Acid.** FR. FICHTER and ELDOR UHL (*Helv. Chim. Acta.*, 1920, 3, 22—39).—According to the literature, the anodic oxidation of toluene and *p*-nitrotoluene at platinum electrodes appears to lead only to the formation of benzaldehyde and *p*-nitrobenzyl alcohol respectively; these results do not appear to harmonise with the powerful oxidising action usually associated with anodic oxygen. Since, also, Fichter and Stocker (*A.*, 1914, i, 947) have found toluquinone among the products of the electrolytic oxidation of toluene, the whole question has been re-examined with particular reference to the substances formed in minor quantity.

The electrolytic oxidation of a suspension of benzaldehyde in 2*N*-sulphuric acid at platinum anodes gave much unchanged material and benzoic acid as the only isolable substances, but the discrepancy between the amounts of original and final material pointed to a further oxidation of the benzoic acid formed. Direct experiment with the latter substance showed that it is actually converted into catechol, quinol, 2:5-dihydroxybenzoic acid, and a hydroxyquinolcarboxylic acid. The latter substances possibly owe their origin to the intermediate production of *o*- and *p*-hydroxybenzoic acids, and, under the experimental conditions, salicylic acid was found to yield quinolcarboxylic acid, whilst *p*-hydroxybenzoic acid gave protocatechuic acid. The production of quinolcarboxylic acid is also observed in the electrolytic oxidation of benzaldehyde and toluene.

Measurements of potential with toluene, benzyl alcohol, benzaldehyde, and benzoic acid, respectively, show a rapid and remarkable increase of anodic polarisation in the case of the aldehyde; the same phenomenon is observed to a much smaller degree with benzyl alcohol and toluene, whilst with benzoic acid, anodic polarisation is very feeble; the results show that it is impossible so to control electrolytic oxidation that only benzyl alcohol is produced, and also that benzoic acid can be further oxidised even in the presence of an excess of toluene. The peculiar behaviour of benzaldehyde is attributed to the formation of a peroxide, presumably either dibenzylidene peroxide hydrate or dibenzylidene peroxide, since evidence of the production of the volatile benzoic peracid,  $\text{Ph}\cdot\text{CO}_3\text{H}$ ,



could not be obtained. The electrolytic oxidation of toluene thus follows the lines of the scheme on the previous page. H. W.

**A New Method of Synthesis of Indenic Ketones.** A. ORÉKHOFF (*Bull. Soc. chim.*, 1919, [iv], **25**, 597—598).—An application of the method previously described for the synthesis of indene derivatives (compare A., 1914, i, 265). When benzylidene-deoxybenzoin dibromide is heated at 140—145°, it loses two molecules of hydrogen bromide and gives diphenylindone, m. p. 151—152°; this yields a *phenylhydrazone*, m. p. 175—176°.

W. G.

**Action of Cyanogen and its Haloids on Mixed Organo-magnesium Derivatives. New Methods of Synthesis of Nitriles and Ketones. New Method of Introduction of a Halogen into an Organic Molecule.** V. GRIGNARD, E. BELLET, and CH. COURTOT (*Ann. Chim.*, 1919, [ix], **12**, 364—393. Compare A., 1916, i, 487).—The first part of the paper is a more detailed account of work already published (compare A., 1911, i, 292; 1912, i, 623; 1914, i, 391). By using 2 mols. of the magnesium alkyl or aryl haloid to 1 mol. of cyanogen chloride, a ketimine results which, when hydrolysed with water or dilute hydrochloric acid, gives the corresponding ketone (A., 1914, i, 391). In this way, the authors have prepared benzophenone, 4:4'-dimethylbenzophenone, 2:2'-dimethylbenzophenone, m. p. 72°, giving an *oxime*, m. p. 105°,  $\alpha\alpha$ -dinaphthyl ketone, 2:4-dimethylbenzophenone, and phenyl  $\alpha$ -naphthyl ketone.

W. G.

**Derivatives of Naphthyl- $\beta$ -ethylamine.** ANTONIO MADINA-VEITIA (*Bull. Soc. chim.*, 1919, [iv], **25**, 601—610; *Anal. Fis. Quim.*, 1918, **16**, 543—545).—The author has prepared a number of naphthalene derivatives having a side-chain with an amino-group in the  $\beta$ -position with the view of studying their action on the sympathetic nervous system in comparison with that of  $\beta$ -methylamino- $\alpha$ -phenylethane and its derivatives.

$\alpha$ -Chloro- $\beta$ -bromo- $\alpha$ -methoxyethane when added to a solution of magnesium in bromobenzene and ether gives  $\beta$ -bromo- $\alpha$ -methoxy- $\alpha$ -phenylethane, b. p. 125—127°/15 mm., which when heated with methylamine in benzene solution at 100° for three hours gives  $\beta$ -methylamino- $\alpha$ -methoxy- $\alpha$ -phenylethane, b. p. 105—106°/22 mm., giving a *hydrochloride* and a *platinichloride*, m. p. 189° (decomp.).  $\beta$ -Methylamino- $\alpha$ -methoxy- $\alpha$ -naphthylethane is similarly prepared, with the intermediate formation of  $\beta$ -bromo- $\alpha$ -methoxy- $\alpha$ -naphthylethane, b. p. 185—190°/14 mm., and gives a *hydrochloride* and a *platinichloride*.

$\alpha$ -Naphthyl methyl ketone, when acted on by amyl nitrite in the presence of sodium ethoxide, gives  $\alpha$ -naphthyl nitrosomethyl ketone, giving a *sodium salt*, and this nitroso-derivative, when reduced with stannous chloride and hydrochloric acid, yields  $\alpha$ -naphthyl aminomethyl ketone,  $C_{10}H_7 \cdot CO \cdot CH_2 \cdot NH_2$ , giving a *hydrochloride*.

Similarly, 4-methoxy- $\alpha$ -naphthyl methyl ketone gives a *nitroso-derivative*, which on reduction yields 4-methoxy- $\alpha$ -naphthyl amino-methyl ketone, isolated as its *hydrochloride*, which when heated in a sealed tube for four hours at 100° with fuming hydrochloric acid gives 4-hydroxy- $\alpha$ -naphthyl aminomethyl ketone, isolated as its *hydrochloride*.

The vaso-constrictive action of these substances has been studied by Trendelenburg's method. It is shown that the introduction of a methoxy-group into the side-chain has little or no influence on the physiological action of the substance, but the replacement of the phenyl nucleus by a naphthyl nucleus has a very marked effect, increasing the vaso-constrictive action about forty times in the case of the substances studied. 4-Hydroxy- $\alpha$ -naphthyl aminomethyl ketone possesses a very marked vaso-constrictive action, which is much greater than that of the corresponding derivative without the hydroxyl group or than that of the corresponding derivative without the carbonyl group in the side-chain. W. G.

### The Constitution of Dypnopinacone and its Derivatives.

**IV. The Luteo-dypnopinacones.** MAURICE DELACRE (*Ann. Chim.*, 1919, [ix], **12**, 394—425. Compare A., 1914, i, 1068; 1916, i, 479; 1918, i, 539; this vol., i, 165).—A more detailed account of work already published (compare A., 1891, 456; 1896, i, 662).

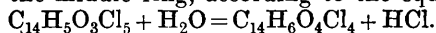
W. G.

[**Preparation of**] *p*-Benzoquinone from Benzene. J. M. WEISS and C. R. DOWNS (U.S. Pat. 1318631).—A mixture of benzene and oxygen or air in the form of vapour or spray is passed over pumice impregnated with vanadium oxide and heated at 300—700°. *p*-Benzoquinone, maleic acid, and by-products are obtained, together with unchanged benzene. As substitutes for the catalyst, vanadium or vanadium compounds, molybdenum, tungsten, gold, ruthenium, cobalt, or the oxides of copper, manganese, cobalt, lead, chromium, antimony, cadmium, and thorium, may be used. The reaction may be carried out at pressures greater than, equal to, or less than atmospheric pressure. After removal of maleic acid by crystallisation or by solution in water, the remaining liquid products may be again passed over the catalyst to effect further oxidation, with the production of additional *p*-benzoquinone and maleic acid. CHEMICAL ABSTRACTS.

**A Novel Degradation in the Anthraquinone Series.** K. FRIES and E. AUFFENBERG (*Ber.*, 1920, **53**, [B], 23—28).—When the hydrochloride of 1-aminoanthraquinone is exhaustively chlorinated in glacial acetic acid, it yields 2:2:3:4:4-pentachloro-1-keto-1:2:3:4-tetrahydroanthraquinone,  $C_6H_4$   $\begin{array}{c} \diagup CO \cdot C \cdot CO \text{---} CCl_2 \\ \diagdown CO \cdot C \cdot CCl_2 \cdot CHCl \end{array}$ , which crystallises in rhombic tablets, m. p. 166—168° (slight decomp.), and may be reduced by stannous chloride to 2:4-dichloro-1-hydroxyanthraquinone, slender, orange-coloured needles, m. p.

242°. The compound may also be reduced by boiling an acetic acid solution with ammonium chloride, the product being 2:3:4-trichloro-1-hydroxyanthraquinone, which crystallises in orange needles, m. p. 214°, forms sparingly soluble, brilliant red alkali salts, and is remarkably stable towards chlorine or concentrated nitric and sulphuric acids.

The pentachloro-derivative undergoes a novel hydrolysis when warmed with concentrated sulphuric acid, the product being o-2:3:4:6-tetrachloro-5-hydroxybenzoylbenzoic acid, formed by the rupture of the middle ring, according to the equation

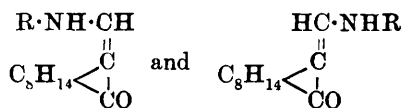


It crystallises in minute druses, m. p. 277—278°, forms a sparingly soluble sodium salt and an *acetate*, m. p. 213°, and is hydrolysed by heating at a higher temperature with sulphuric acid to phthalic acid and 2:3:4:5-tetrachlorophenol. The same derivative of benzoylbenzoic acid is formed as a by-product when the original, crude chlorination product, containing ammonium chloride, is boiled with acetic acid, but it is not given by the main product of this reaction, namely, the above trichlorohydroxyanthraquinone.

J. C. W.

### Stereoisomeric Derivatives of Aminomethylenecamphor.

I. HANS RUPE, MAX SEIBERTH, and WALTER KUSSMAUL (*Helv. Chim. Acta*, 1920, **3**, 50—70).—Aminomethylenecamphor and many of its derivatives are found to exist in two forms, characterised by lower melting point and generally greater solubility, and higher melting point and usually more sparing solubility; these are designated  $\beta$ - and  $\alpha$ -compounds respectively. In general, they are readily mutually transformable. Since a new asymmetric carbon atom is not developed during the formation of these substances, optical isomerism is out of the question, and it appears certain that instances of *cis-trans*-isomerism (annexed formula) are being dealt



with, although direct experimental evidence on this point is lacking. The optical investigation of these substances promises results of considerable interest, since but few optically active *cis-trans*-isomerides have been examined; the sparing solubility of the products at the ordinary temperature and the ease with which they undergo transformation when the temperature is raised have prevented an extended examination, and the results which have been obtained so far do not allow any general conclusions to be drawn.

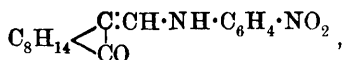
A considerable improvement in the preparation of hydroxymethylenecamphor is effected if the sodium camphor is prepared by the interaction of camphor and sodamide in benzene solution; under these conditions, the formation of borneol is avoided, and any unattacked camphor can be recovered.

$\alpha$ -Aminomethylenecamphor is conveniently prepared by heating

hydroxymethylenecamphor with saturated aqueous ammonia under pressure at  $100^\circ$ ; it forms colourless, shining leaflets, m. p.  $156^\circ$ ,  $D_4^{20}$   $0.8176$ ,  $[\alpha]_D^{20} + 191.37^\circ$ ,  $[\alpha]_B^{20} + 257.32^\circ$ ,  $[\alpha]_{Hg}^{20} + 323.41^\circ$ ,  $[\alpha]_F^{20} + 477.19^\circ$ ,  $[\alpha]_F/[\alpha]_C$   $2.48$  in alcoholic solution. When distilled under diminished pressure, it is quantitatively converted into the  $\beta$ -form, m. p.  $103$ — $104^\circ$ ,  $D_4^{20}$   $0.8159$ ,  $[\alpha]_C^{20} + 236.57^\circ$ ,  $[\alpha]_B^{20} + 313.76^\circ$ ,  $[\alpha]_E^{20} + 388.23^\circ$ ,  $[\alpha]_F^{20} 553.99^\circ$ ,  $[\alpha]_F/[\alpha]_C$   $2.34$ . The latter is very labile, but can be preserved unchanged in substance, even if exposed to sunlight; it is converted into the  $\alpha$ -form if its solution in alcohol or benzene is evaporated, when the benzene solution is exposed to sunlight, or when the alcoholic solution is boiled.

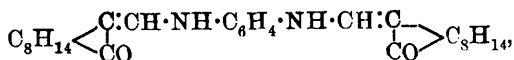
$\alpha$ -Benzoylaminoethylenecamphor is the sole product of the action of benzamide on hydroxymethylenecamphor in glacial acetic acid solution, and is formed, together with the  $\beta$ -isomeride, by the benzylation of aminomethylenecamphor in pyridine solution; it forms slender, colourless needles, m. p.  $208^\circ$ ,  $D_4^{20}$   $0.9838$ ,  $[\alpha]_C^{20} + 164.28^\circ$ ,  $[\alpha]_B^{20} + 219.29^\circ$ ,  $[\alpha]_{Hg}^{20} + 273.15^\circ$ ,  $[\alpha] + 393.06^\circ$ ,  $[\alpha]_F/[\alpha]_C$   $2.39$  in pyridine solution. The  $\beta$ -modification crystallises in monoclinic prisms  $[a:b:c=0.96402:1:1.05011, \beta=110^\circ 40']$ , m. p.  $112^\circ$ ,  $D_4^{20}$   $0.9835$ ,  $[\alpha]_C^{20} + 166.44^\circ$ ,  $[\alpha]_B^{20} + 228.29^\circ$ ,  $[\alpha]_{Hg}^{20} + 292.67^\circ$ ,  $[\alpha]_F^{20} + 453.11^\circ$ ,  $[\alpha]_F/[\alpha]_C$   $2.72$ ; it is converted into the  $\alpha$ -variety when its solution in light petroleum is exposed to ultra-violet light, but not by treatment with hydrogen chloride in alcoholic or light petroleum solution. The reverse transformation is effected by boiling a solution of the  $\alpha$ -form in pyridine.

$\alpha$ - and  $\beta$ -*p*-Nitroanilinomethylenecamphor,

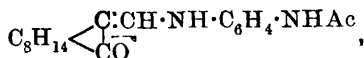


are simultaneously formed by the action of *p*-nitroaniline on hydroxymethylenecamphor in glacial acetic acid solution, and are separated by taking advantage of the greater solubility of the  $\beta$ -isomeride in cold benzene. The  $\alpha$ -form crystallises in canary-yellow leaflets, m. p.  $180$ — $181^\circ$ , and slowly passes into the  $\beta$ -isomeride at the ordinary temperature, rapidly at  $200^\circ$ ; the  $\beta$ -isomeride forms orange-yellow needles with a violet reflex, m. p.  $151$ — $152^\circ$ , and is converted into the  $\alpha$ -form when its solution in boiling alcohol is exposed to direct sunlight.

*p*-Phenylenediaminodimethylenecamphor,



pale yellowish-green, microscopic needles, m. p.  $276$ — $277^\circ$ , appears to be the sole product of the action of *p*-phenylenediamine on hydroxymethylenecamphor; it could only be obtained in one form. *p*-Acetylaminodimethylenecamphor,



forms pale yellowish-green leaflets, m. p. 226—227°, and exists in one form only. *p*-Aminoanilinomethylenecamphor could not be obtained by the reduction of the corresponding nitro-compound by iron and acetic acid; although reduction appears to occur, the amino-derivative is immediately hydrolysed, and condensation then occurs between the *p*-phenylenediamine and hydroxymethylenecamphor, which are thus formed with the ultimate production of *p*-phenylenediaminodimethylenecamphor; reduction could not be effected with ammonium sulphide, whilst with sodium sulphide either form of the nitro-compound yields the same amino-derivative in poor yield. The pure amine, m. p. 163°, is, however, obtained by the action of ethyl-alcoholic potassium hydroxide on the corresponding acetyl derivative. The *hydrochloride* is sparingly soluble in water and cannot be diazotised.

*p*-Phenetidinomethylenecamphor ( $\beta$ -form, coarse plates and prisms, m. p. 111—112°;  $\alpha$ -form, pale yellowish-green leaflets, m. p. 166—167°) is prepared by the action of *p*-phenetidine on hydroxymethylenecamphor in alcoholic solution, and is separated into its isomerides by fractional crystallisation from benzene. The  $\beta$ -variety is very labile, and is converted into the  $\alpha$ -variety when attempts are made to recrystallise it from alcohol; it has not been found possible to effect the reverse transformation. H. W.

### Stereoisomeric Derivatives of Aminomethylenecamphor.

II. HANS RUPE, MAX SEIBERTH, and WALTER KUSSMAUL (*Helv. Chim. Acta*, 1920, **3**, 71—89).—A continuation of the work described in the preceding abstract.

*Diethylaminomethylenecamphor*,  $C_8H_{14} \begin{smallmatrix} \diagup \\ \text{C} \cdot \text{CH} \cdot \text{NEt}_2 \\ \diagdown \\ \text{CO} \end{smallmatrix}$ , is obtained

as a pale yellow, viscous oil, b. p. 175—175.5°/11 mm., which solidifies when cooled to a mass of transparent plates, m. p. 20—22°, by the action of diethylamine on hydroxymethylenecamphor or chloromethylenecamphor. The *hydrochloride* is slowly decomposed in aqueous solution, yielding hydroxymethylenecamphor and diethylamine hydrochloride. *Piperidinomethylenecamphor* is a pale yellow, viscous oil, b. p. 203—204°/11 mm., m. p. 60° after softening at 58°; the *hydrochloride*, slender needles, suffers first dissociation and then hydrolysis in aqueous solution. *Tetrahydroquinolinomethylenecamphor* forms coarse, transparent prisms, m. p. 109°. *Carbamidomethylenecamphor*,  $C_8H_{14} \begin{smallmatrix} \diagup \\ \text{C} \cdot \text{CH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2 \\ \diagdown \\ \text{CO} \end{smallmatrix}$ ,

prepared by melting the components together or by condensation in glacial acetic acid solution, crystallises in needles, m. p. 197°; a second modification, which does not melt below 280°, possibly exists.  $\beta$ -Ethylurethanomethylenecamphor is exclusively obtained when its components are heated together at 110°, and forms a colourless, odourless, highly refractive oil, which does not solidify in a mixture of ice and salt, and rapidly becomes yellow or red when preserved; it has b. p. 178—179°/10 mm.,  $D_4^{20}$  0.9835,  $[\alpha]_D^{20} + 145.93^\circ$ ,  $[\alpha]_D^{20} + 197.17^\circ$ ,  $[\alpha]_{H\beta}^{20} + 247.62^\circ$ ,  $[\alpha]_F^{20} + 366.69^\circ$ ,  $[\alpha]_F/[\alpha]_C$



2.51 in pyridine solution. When, however, the components are mixed in glacial acetic acid solution, the  $\alpha$ -variety is mainly formed at the ordinary temperature, but the reaction is very incomplete, whilst at a higher temperature reaction proceeds quantitatively, but yields more of the  $\beta$ -variety. The  $\alpha$ -isomeride forms colourless, many-sided crystals, m. p.  $162^\circ$ ,  $D_4^{20}$  0.93352,  $[\alpha]_C^{20} + 149.42^\circ$ ,  $[\alpha]_D^{20} + 198.52^\circ$ ,  $[\alpha]_{Hg}^{20} + 245.11^\circ$ ,  $[\alpha]_F^{20} + 347.35^\circ$ ,  $[\alpha]_F/[\alpha]_C$  2.32. Transformation of the  $\beta$ - into the  $\alpha$ -variety can be effected by hydrogen bromide, hydrogen chloride, concentrated sulphuric acid, nitrous fumes, iodine in ethereal solution, by exposure to direct sunlight, and by preservation in the dark. The reverse action is effected by boiling a solution of the  $\alpha$ -variety in glacial acetic acid with exclusion of light.

The two forms of *ethyl methylenecamphor-p-aminobenzoate* are simultaneously formed by the condensation of the components in glacial acetic acid solution, and are separated with the aid of light petroleum; the  $\alpha$ -variety crystallises in minute needles, m. p.  $176^\circ$ , whilst the  $\beta$ -form has m. p.  $105^\circ$ . The former modification is exclusively formed when a mixture of the components is gently heated; it appears to be exceptionally stable, but undergoes partial transformation when its solution in formic acid is boiled during a protracted period in direct sunlight and in the presence of iodine.

The *methylenecamphoranthranilic acids* are simultaneously formed from hydroxymethylenecamphor and anthranilic acid in glacial acetic acid solution, and can be separated to some extent mechanically, owing to the difference in their crystalline forms. Separation by means of solvents is impracticable, owing to their very similar solubilities. Isolation of the  $\beta$ -variety is best effected by boiling the mixture of isomerides with benzene, when the  $\alpha$ -variety passes into the  $\beta$ -form, almost colourless needles, which rapidly become brown, and have m. p.  $112^\circ$  and  $176^\circ$  after re-solidifying. The  $\alpha$ -variety is conveniently obtained by boiling a solution of the  $\beta$ -form in toluene, and forms pale brown, many-sided crystals, m. p.  $176^\circ$ ; the latter isomeride is exclusively formed when the components are heated together, the result being attributable to the high temperature of the reaction. Attempts to convert the methylenecamphoranthranilic acids into indole or indigo-derivatives were unsuccessful. Acetic anhydride, however, converts the  $\beta$ -derivative into *methylenecamphor-N-acetylanthranilic acid*,

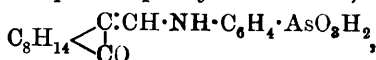
$C_8H_{14} \begin{smallmatrix} \diagup C:CH \cdot NAc \cdot C_6H_4 \cdot CO_2H \\ \diagdown CO \end{smallmatrix}$ , colourless, shining needles united

in clusters, m. p.  $185^\circ$ , to an intensely green liquid, which gradually becomes reddish-brown. Either variety is transformed by phosphoryl chloride into the  $\beta$ -lactam of methylenecamphor-

anthranilic acid,  $C_6H_4 \begin{smallmatrix} \diagup N \cdot CH : C \\ \diagdown CO \quad OC \end{smallmatrix} C_8H_{14}$ , colourless crystals, which

immediately become discoloured on exposure to air and have m. p.  $165^\circ$ . The substance is converted by boiling water into methylenecamphoranthranilic acid, and by cold alkali into a mixture of the sodium salts of the two forms of the acid.

*Methylenecamphor-p-aminophenylarsinic acid*,



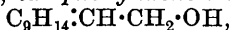
is best obtained as *sodium* salt by heating hydroxymethylenecamphor with atoxyl at  $110^\circ$ ; it forms slender, colourless needles, which decompose at  $220^\circ$  and melt indistinctly at  $250^\circ$ ; anilino-methylenecamphor, m. p.  $168-170^\circ$ , and a substance,  $\text{C}_{27}\text{H}_{42}\text{O}_2$ , slender, yellow needles, m. p.  $188^\circ$ , are formed as by-products during the condensation.

H. W.

**Transpositions in the Camphene Series.** G. LANGLOIS (*Ann. Chim.*, 1919, [ix], 12, 265—363. Compare this vol., i, 171). —By the direct bromination of camphene in anhydrous ether,  $\omega$ -bromocamphene, b. p.  $115-120^\circ/15$  mm.,  $225-226^\circ/760$  mm.,  $D^{15}_4 1.265$ ,  $[\alpha]_D + 68.85^\circ$ , is obtained, its constitution being proved by its behaviour on oxidation either by nitrous vapour or by potassium permanganate, camphenylone being the product in either case. In the preparation of a magnesium derivative from bromocamphene, some *dehydrodicamphene*,  $\text{C}_{10}\text{H}_{15} \cdot \text{C}_{10}\text{H}_{15}$ , m. p.  $181^\circ$ , is obtained. The magnesium derivative when acted on by carbon dioxide gives an *acid*,  $\text{C}_{10}\text{H}_{15} \cdot \text{CO}_2\text{H}$ , m. p.  $124-125^\circ$ , which on oxidation also gives camphenylone and oxalic acid.  $\omega$ -Bromocamphene is stable towards Beckmann's oxidising mixture, and with hydrogen bromide yields 2- $\omega$ -dibromocamphane, the latter change being reversible. Attempts to replace the bromine in bromocamphene with a phenyl group by means of magnesium phenyl bromide were not very successful, whilst with magnesium methyl iodide the product was cymene. On chlorination in ether, bromocamphene gives *dichlorobromocamphene*,  $\text{C}_{10}\text{H}_{15}\text{Cl}_2\text{Br}$ , m. p.  $74^\circ$ . Hydrogen chloride in the cold is without action on bromocamphene, but when passed into an acetic acid solution at  $100^\circ$  it yields dibromocamphane. As compared with camphene, bromocamphene only undergoes very slow acetylation, and the product is not characterised.

By carefully restricted chlorination of camphene, a certain amount of chlorocamphene, b. p.  $95-98^\circ/15$  mm.,  $D^{15}_4 1.016-1.017$ ,  $[\alpha]_D + 37^\circ$ , is obtained, which is not acted on by any hydrogen chloride or by Beckmann's oxidising agent. With potassium permanganate, it is oxidised to camphenylone. With hydrogen bromide, it gives  $\omega$ -chloro-2-bromocamphane, m. p.  $103^\circ$ , and on further chlorination it gives trichlorocamphene, m. p.  $104^\circ$ . On bromination it gives *chlorodibromocamphene*,  $\text{C}_{10}\text{H}_{15}\text{ClBr}_2$ , m. p.  $64-65^\circ$ .

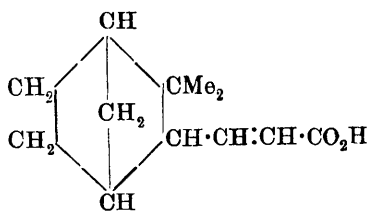
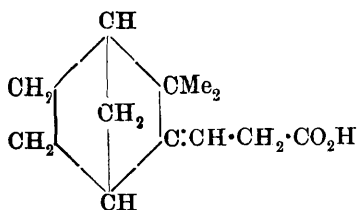
When camphene is heated on an oil-bath for two days with a mixture of trioxymethylene and acetic acid, it gives an *acetate*,  $\text{C}_{11}\text{H}_{17} \cdot \text{CO}_2 \cdot \text{CH}_3$ , b. p.  $130-135^\circ/20$  mm., which on hydrolysis gives a primary alcohol, *camphenylidene-6-ethanol*,



b. p.  $125-126^\circ/8$  mm.,  $135^\circ/17$  mm.,  $234-238^\circ/760$  mm.,  $D^{15}_4 0.987-0.988$ ,  $[\alpha]_D + 45^\circ$ , which is best purified through its *hydrogen phthalate*,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{C}_{11}\text{H}_{17}$ , m. p.  $124-125^\circ$ . If the alcohol is subjected to prolonged heating with alcoholic potassium

hydroxide, it gives an *ether*,  $O(CH_2 \cdot CH \cdot C_9H_{14})_2$ , b. p. 235—240°/25 mm.,  $D^{20}_D$  0.983. The alcohol,  $C_{11}H_{17} \cdot OH$ , when oxidised with potassium permanganate in the presence of aqueous sodium carbonate, gives camphenylone, hydroxycamphenylanic acid, and oxalic acid. In the presence of sodium hydroxide, the products of oxidation are camphenylone, camphenecamphoric acid, and oxalic acid. By a similar study of the oxidation of camphene, it is shown that the endocyclic transposition is not due to the permanganate, but rather to the isomerising action of the free alkali used in excess. Certain derivatives of camphenylidene-6-ethanol have been prepared. It gives a *diphenylurethane*, difficult to purify, and a *pyruvate*, b. p. 150—155°/10 mm., giving a *semicarbazone*, m. p. 167°. The ether,  $(C_{11}H_{17})_2O$ , when oxidised by sodium dichromate and sulphuric acid, gives first an aldehyde, and then camphenylidene-ethanoic acid.

A *chloride*,  $C_{11}H_{17}Cl$ , corresponding with camphenylidene-6-ethanol, may be obtained either by the action of hydrogen chloride on the alcohol in toluene solution at 140—150°, or by the action of phosphorus pentachloride either on the alcohol or the corresponding ether. This chloride has b. p. 100—102°/6 mm., 110°/15 mm.,  $D^{15}_D$  1.020,  $[\alpha]_D + 27.38^\circ$ . On oxidation with potassium permanganate, it yields camphenylone. Unlike  $\omega$ -chlorocamphene, it is oxidised by sodium dichromate and sulphuric acid, giving first an aldehyde and then camphenylideneacetic acid. The chloride is quite stable towards either hydrogen chloride or hydrogen bromide, undergoing no transposition. Further, it is not reduced by sodium in absolute alcohol, but under these conditions simply gives an *ethyl ether*,  $C_{10}H_{17} \cdot OEt$ , b. p. 125—130°/8 mm., 230°/760 mm. This ether, when oxidised by the chromic acid mixture gives camphenylideneacetic acid. If the reduction of the chloride is carried out by zinc and hydrochloric acid, the product is  $\omega$ -*methylcamphene*, b. p. 178°,  $D^{15}_D$  0.884,  $[\alpha]_D + 4.28^\circ$ . The chloride,  $C_{11}H_{17}Cl$ , when acted on by sodium or magnesium in anhydrous ether, gives a *terpenic hydrocarbon*,  $C_{11}H_{17} \cdot C_{11}H_{17}$ , b. p. 210°/25 mm.,  $D^{15}_D$  0.952,  $[\alpha]_D + 67.30^\circ$ , which is remarkably stable towards aqueous potassium permanganate. By the action of sodium ethoxide, the chloride yields the corresponding ether,  $(C_{11}H_{17})_2O$ , described above. With sodium cyanide, the chloride yields the *nitrile*,  $C_{11}H_{17} \cdot CN$ , b. p. 140°/12 mm.,  $D^{15}_D$  0.959,  $D^{20}_D$  0.963,  $[\alpha]_D + 61.20^\circ$ , which is readily oxidised to camphenylone, and on hydrolysis gives the corresponding *acid*,  $C_{11}H_{17} \cdot CO_2H$ , m. p. 100°.

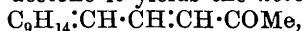


b. p.  $185^{\circ}/24$  mm.,  $[\alpha]_D +41.16^{\circ}$ . From its behaviour on oxidation, it is suggested that this acid is really a mixture of two  $\alpha$ - and  $\beta$ -isomerides (see formulæ on previous page). When camphenylidene-6-ethanol is oxidised by Beckmann's mixture in the cold, it yields *camphenylidene-6-acetaldehyde*,  $C_9H_{14}:CH:CHO$ , b. p.  $130^{\circ}/12$  mm.,  $124^{\circ}/8$  mm.,  $D^{15} 1.002$ ,  $[\alpha]_D +72.58^{\circ}$ , which gives a sodium bisulphite compound, a semicarbazone, m. p.  $233^{\circ}$ , and an oxime, b. p.  $160^{\circ}/15$  mm. The oxime gives a hydrochloride, and on dehydration yields *camphenylideneacetonitrile*,  $C_9H_{14}:CH:CN$ , b. p.  $132^{\circ}/6$  mm.,  $140^{\circ}/10$  mm.,  $D^{15} 0.987$ ,  $D^{20} 0.983$ ,  $[\alpha]_D +110^{\circ}$ , which when boiled with alcoholic potassium hydroxide gives the corresponding amide,  $C_{10}H_{15}:CO:NH_2$ , m. p.  $192^{\circ}$ . This amide is very stable, and is not hydrolysed by sulphuric acid. Camphenylidene-acetaldehyde gives a diacetate,  $C_9H_{14}:CH:CH(CO_2Me)_2$ , m. p.  $54-55^{\circ}$ .

If the oxidation of camphenylidene-6-ethanol with Beckmann's mixture is pushed further, the product is *camphenylideneacetic acid*, m. p.  $124-125^{\circ}$ , b. p.  $181^{\circ}/19$  mm., the same acid being obtained by the action of carbon dioxide on the magnesium derivative of  $\omega$ -bromocamphene. It gives an ethyl ester, b. p.  $150^{\circ}/22$  mm.,  $D^{20} 1.008$ , and an acid chloride, b. p.  $145^{\circ}/15$  mm., which by the action of ammonia is converted into the amide, m. p.  $192^{\circ}$  (see above). When heated on an oil-bath for several hours, camphenylideneacetic acid loses carbon dioxide and gives a *camphene*, m. p.  $45-46^{\circ}$ , b. p.  $158-160^{\circ}$ , which on oxidation yields camphor. On oxidation with potassium permanganate, the acid yields camphenylone, and on reduction with sodium in amyl alcohol it gives *isocamphanecarboxylic acid*, which when oxidised gives *r-camphenylanic acid*, m. p.  $75-76^{\circ}$ .

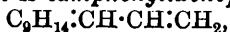
$\omega$ -Methylcamphene may be obtained by the reduction of camphenylideneacetaldehyde by zinc and hydrochloric acid, its constitution being shown by its behaviour on oxidation with potassium permanganate, when it yields camphenylone, oxalic acid, and camphenecamphoric acid. It is not oxidised by sodium dichromate and sulphuric acid, or by hydrogen chloride, but with hydrogen bromide it gives a *hydrobromide*,  $C_{11}H_{19}Br$ , b. p.  $108-110^{\circ}/17$  mm.,  $D^{15} 1.175$ .

Camphenylideneacetaldehyde is capable of condensing with ketones. Thus with acetone it yields the *ketone*,

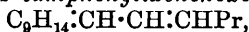


b. p.  $160^{\circ}/12$  mm.,  $D^{15} 0.980$ , giving a *semicarbazone*, m. p.  $220-221^{\circ}$ . With methyl ethyl ketone the aldehyde gives the *ketone*,  $C_9H_{14}:CH:CH:CH:COEt$ , b. p.  $172-175^{\circ}/12$  mm.,  $D^{15} 0.968$ , giving a *semicarbazone*, m. p.  $209-210^{\circ}$ . Owing to the presence of three conjugated double linkings, neither of these ketones is oxidised by chromic acid mixture, and the first-named is not acted on by hypochlorites. Camphenylideneacetaldehyde also reacts with magnesium alkyl haloids of low molecular weight to give unstable secondary alcohols, which, when distilled in a vacuum, give diethylenic hydrocarbons. Thus, with magnesium methyl

iodide, the final product is *camphenyldenepropylene*,



b. p. 85—90°/10 mm., 203—205°/760 mm.,  $D^{15}_D$  0.921,  $D^{20}_D$  0.917,  $[\alpha]_D + 76.39^\circ$ . With magnesium ethyl bromide the product is *camphenyldenebutylene*,  $\text{C}_9\text{H}_{14}:\text{CH}\cdot\text{CH}:\text{CHMe}$ , b. p. 95—97°/12 mm. and 230—232°/760 mm.,  $D^{15}_D$  0.919,  $[\alpha]_D + 70^\circ$ . With magnesium propyl bromide the product is *camphenyldenepentene*,  $\text{C}_9\text{H}_{14}:\text{CH}\cdot\text{CH}:\text{CHEt}$ , b. p. 110—120°/15 mm. and 238—240°/760 mm.,  $D^{15}_D$  0.905,  $[\alpha]_D + 80^\circ$ , and with magnesium butyl bromide the product is *camphenyldenehexene*,



b. p. 140°/10 mm. and 255°/760 mm.,  $D^{15}_D$  0.900,  $[\alpha]_D + 73.5^\circ$ . All these diethylenic hydrocarbons when oxidised with chromic acid mixture give the original aldehyde or camphenyldeneacetic acid. They also undergo spontaneous oxidation, giving camphenyldeneacetaldehyde and formaldehyde, acetaldehyde, propaldehyde, and butaldehyde respectively.

W. G.

**Chemistry of the Terpenes. XIX. Synthesis of a *m*-Menthadiene from *m*-iso-Cymene.** GEORGE GERALD HENDERSON and THOMAS FREDERICK SMEATON (T., 1920, 117, 144—149).

**Occurrence of the Terpene Terpinene in the Oil of *Eucalyptus megacarpa*.** HENRY G. SMITH (J. Proc. Roy. Soc., N.S. Wales, 1918, 52, 529—533).—The oil of *Eucalyptus megacarpa* contains pinene, limonene, and dipentene, about 30% of cineole, and possibly as much as 10% of terpinene. The latter was detected in the fraction boiling from 170—190° by the formation of its nitrosite, m. p. 155°, and by its rapid oxidation in the cold with Beckmann's chromic acid mixture, as evidenced by the increased optical rotation of the residual oil (consisting mainly of limonene) after the removal of the inactive terpinene.

G. F. M.

**The Vulcanisation of Caoutchouc with Agents other than Sulphur.** HENRY P. STEVENS (J. Soc. Chem. Ind., 1917, 35, 107).—Vulcanisation of caoutchouc with from 1 to 4% of dinitrobenzene or trinitrobenzene at 140° is possible in the additional presence of a considerable proportion (for example, 8 to 30%) of lead oxide or magnesium oxide; the trinitro-compound is more effective than its dinitro-analogue, whilst with nitrobenzene itself satisfactory results are not obtainable. The nitro-compound enters almost entirely into combination with the caoutchouc, and is not removable by acetone. The products possess poor mechanical qualities relative to caoutchouc vulcanised in the ordinary way with sulphur. Benzoyl peroxide also effects vulcanisation, and in this case no third substance is necessary; from 4 to 6% of the peroxide is required, and a vulcanisation period of ten to fifteen minutes at 130—135°. The products are weak and have a remarkably pale colour. [See also Bunschoten, A., 1918, i, 503; Ostromisslenski, A., 1916, i, 278.]

D. F. T.

**The Nature of Vulcanisation. I. The Combination of Rubber with Sulphur. II. The Action of Solvents on Vulcanised Rubber.** H. P. STEVENS (*J. Soc. Chem. Ind.*, 1919, 38, 192—196r).—The results on which Harries and Fonrobert (*A.*, 1916, i, 659, 733) base their opinion that vulcanisation of caoutchouc is essentially a physical process, and may occur without any appreciable combination with sulphur, are probably explained by unsuitable conditions of experiment. Under similar conditions, but with the additional precaution of vulcanising the mixture of caoutchouc and sulphur in thin sheets, so as to ensure greater uniformity of heating, and consequently of vulcanisation, the author obtained a product which, after exhaustive extraction with acetone, retained more than 1% of combined sulphur. It is therefore not possible to effect ordinary vulcanisation without the concurrent fixation of an appreciable proportion of sulphur. With an increasing proportion of combined sulphur, caoutchouc becomes less and less soluble in solvents such as benzene; freshly vulcanised samples containing 0.27% and 0.39% of combined sulphur could be dissolved in benzene, whereas 0.45% prevented solution; after storage for three months, none of these samples would pass completely into solution. The extract obtained on treating more highly vulcanised caoutchouc with hot benzene contains the same proportion of combined sulphur as the undissolved residue.

D. F. T.

**Autoxidation of Colophony.** LUDWIG PAUL (*Kolloid Zeitsch.*, 1919, 25, 241—246).—The constituents of colophony are investigated, and some of the products examined and characterised. When a solution of colophony in alkali is treated with hydrochloric acid, a voluminous precipitate of  $\gamma$ -pinic acid is obtained; this substance has m. p. 75—76°, which in eight months rises to about 88°.  $\alpha$ -Pinic acid has a constant m. p. 81—83°, and shows a tendency to form liquid crystals. It is soluble in water and petroleum, as also is  $\gamma$ -pinic acid.  $\beta$ -Pinic acid melts at 98—100° (compare *A.*, 1918, i, 411).

J. F. S.

**Compounds of High Molecular Weight. I. Synthesis of some Acylglucosides of High Molecular Weight.** SVEN ODÉN (*Arkiv Kem. Min. Geol.*, 1917, 6, No. 18).—Almost all known organic compounds of high molecular weight are natural products of indefinite constitution and extremely difficult to purify, circumstances which are great obstacles to the study of their physico-chemical properties. The author has now synthesised a series of esters of 2:4:6-tribromophenol-*d*-glucoside with a view to a study of the variation of their properties with molecular weight. The esters were prepared by E. Fischer's process, for which the most suitable conditions in this case consist in treating a suspension of the finely divided glucoside in dry chloroform with excess (about one-third) of the acid chloride and quinoline at about 50°. The product was usually isolated by precipitation from the solution by

alcohol, and purified by repetition of the treatment, the bromine content furnishing an effective criterion of purity. The constancy of melting point of the products renders it improbable that the use of quinoline caused any stereoisomeric change during the reaction. All the products were stable, indifferent substances, and slightly laevorotatory. With the exception of the tetrapropionate, the tetrabenzoate, and the tetra-*p*-bromobenzoate, which are crystalline, they were amorphous substances resembling stearin or fats, and in their aspect and solubility relationships lipid in character. It is noteworthy that the tetrabenzoate exists in two interconvertible forms, an amorphous form, m. p.  $94^{\circ}$ , and a crystalline, m. p.  $147^{\circ}$ , the difference in m. p. being apparently conditioned by the variation in granular size (compare Pawlov, A., 1910, ii, 1033).

The following derivatives of 2:4:6-tribromophenol-*d*-glucoside are described: the *tetra*-acetate,  $C_{20}H_{21}O_{10}Br_3$ , needle-shaped crystals, m. p.  $195$ — $196^{\circ}$ ; the *tetrapropionate*,  $C_{24}H_{29}O_{10}Br_3$ , prisms, m. p.  $89.5^{\circ}$ ; the *tetralaurate*,  $C_{60}H_{101}O_{10}Br_3$ , resembling fat, m. p.  $48$ — $49^{\circ}$ ; the *tetramyristate*,  $C_{68}H_{117}O_{10}Br_3$ , m. p.  $56$ — $57^{\circ}$ ; the *tetrapalmitate*,  $C_{76}H_{133}O_{10}Br_3$ , resembling stearin, m. p.  $61$ — $62^{\circ}$ ; the *tetrastearate*,  $C_{84}H_{149}O_{10}Br_3$ , resembling stearin, m. p.  $70$ — $71^{\circ}$ , in tetrachloroethane solution,  $[\alpha]_D^{20} -3.6^{\circ}$ ; the *tetrahexabromostearate*,  $C_{84}H_{125}O_{10}Br_{27}$ , fairly hard, m. p.  $152^{\circ}$ ; the *tetracerotate*,  $C_{116}H_{213}O_{10}Br_3$ , solid, m. p.  $80$ — $81^{\circ}$ ; the *tetrabenzoate*,  $C_{40}H_{29}O_{10}Br_3$ , m. p. as above; the *tetra-p*-bromobenzoate,  $C_{40}H_{25}O_{10}Br_7$ , m. p.  $115^{\circ}$  amorphous,  $214^{\circ}$  crystalline (aggregates of needle-shaped crystals); the *tri-β*-naphthoate,  $C_{45}H_{81}O_9Br_3$ , m. p.  $175^{\circ}$ ; the *tetra-β*-naphthoate,  $C_{56}H_{87}O_{10}Br_3$ , m. p.  $218^{\circ}$ .

In addition, the following were prepared from *α*-methyl-*d*-glucoside: the *tripalmitate*,  $C_{65}H_{104}O_9$ , amorphous, m. p.  $77^{\circ}$ ; the *tristearate*,  $C_{61}H_{108}O_9$ , amorphous, m. p.  $82^{\circ}$ ; the *tetrastearate*,  $C_{79}H_{150}O_{10}$ , amorphous, m. p.  $68^{\circ}$ ; the *tetra-p*-bromobenzoate,  $C_{35}H_{26}O_{10}Br_4$ , needles, m. p.  $148^{\circ}$ .

J. K.

### Compounds of High Molecular Weight. II. Some Acyl Derivatives of Natural Glucosides of High Molecular Weight.

SVEN ODÉN (*Arkiv Kem. Min. Geol.*, 1918—1919, 7, No. 15, 1—22).—The method of acylation previously described (see previous abstract) gives good results when applied to natural glucosides, and has the advantage over older methods of giving completely acylated products. In several cases the products were crystalline, with a sharp melting point, but the granular size was again observed to have a distinct influence on the melting point; in all cases this was depressed by precipitation of the amorphous or microcrystalline form by alcohol from a solution of the crystalline form in chloroform. The chlorides of *β*-naphthalene- and *α*-bromocamphor-*π*-sulphonic acids were also used, this being the first occasion on which sulpho-derivatives of members of the sugar group have been prepared. In these cases, however, a temperature above  $50^{\circ}$  was necessary for the condensation, the reaction proceeded less smoothly,

the resulting compounds were impure, and the yields only about 30%. The products were very friable, and appeared under the microscope as small, strongly refractive, glassy spheres. In the impure condition, they are not dissimilar from the oxidation products of sulphite liquors. The following derivatives are described.

*Salicin*:—*pentacinnamate*,  $C_{58}H_{48}O_{12}$ , needles, m. p.  $173^{\circ}$ ,  $[\alpha]_D^{19} + 46.5^{\circ}$ , *pentaphenylpropionate*,  $C_{58}H_{58}O_{12}$ , long needles, m. p.  $58^{\circ}$ ,  $[\alpha]_D^{18} - 3.5^{\circ}$ , and *penta-p-bromobenzoate*,  $C_{48}H_{33}O_{12}Br_5$ , needles, m. p.  $158^{\circ}$ ,  $[\alpha]_D^{19} + 30.2^{\circ}$ .

*Helicin*:—*tetracinnamate*,  $C_{49}H_{40}O_{11}$ , prisms, m. p.  $176^{\circ}$ ,  $[\alpha]_D^{18} + 77.3^{\circ}$  (*p-bromophenylhydrazone*,  $C_{55}H_{45}O_{10}N_2Br$ , amorphous, m. p.  $118-120^{\circ}$ , decomp.), *tetrapalmitate*,  $C_{77}H_{136}O_{11}$ , amorphous, m. p.  $68^{\circ}$  (*p-bromophenylhydrazone*,  $C_{83}H_{141}O_{10}N_2Br$ , amorphous, m. p. ca.  $45^{\circ}$ ).

*Coniferin*:—*pentacinnamate*,  $C_{61}H_{52}O_{13}$ , amorphous, m. p. ca.  $145^{\circ}$ , and *tetratearate*,  $C_{88}H_{158}O_{12}$ , amorphous, m. p.  $69-70^{\circ}$ .

*Amygdalin*:—*heptabenzoate*,  $C_{69}H_{55}O_{18}N$ , small needles, m. p.  $218^{\circ}$ ,  $[\alpha]_D^{18} - 10.5^{\circ}$ , *hepta-p-chlorobenzoate*,  $C_{69}H_{48}O_{18}NCl_7$ , crystals, m. p.  $234^{\circ}$ , slightly laevorotatory, *hepta-p-bromobenzoate*,

$C_{69}H_{48}O_{18}NBr_7$ , needles, m. p.  $229^{\circ}$ , *hepta-anisate*,  $C_{76}H_{69}O_{25}N$ , amorphous, m. p.  $117-119^{\circ}$ ,  $[\alpha]_D^{20} + 13.2^{\circ}$ , and *heptastearate*,  $C_{146}H_{265}O_{18}N$ , amorphous, m. p.  $92^{\circ}$ ,  $[\alpha]_D^{18.5} - 8.40^{\circ}$ .

*Phloridzin*:—*hepta-p-bromobenzoate*,  $C_{70}H_{45}O_{17}Br_7$ , amorphous, m. p.  $130-132^{\circ}$ ,  $[\alpha]_D^{19} + 19.5^{\circ}$ , and *heptapalmitate*,  $C_{133}H_{231}O_{17}$ , amorphous, m. p.  $51^{\circ}$ ,  $[\alpha]_D^{18.5} - 9.55^{\circ}$ .

*$\alpha$ -Methyl-d-glucoside*:—*tetra- $\beta$ -naphthalenesulphonate*,  $C_{47}H_{36}O_{14}S_4$ , snow-white powder, m. p.  $147^{\circ}$ , *tetra- $\alpha$ -bromocamphor- $\pi$ -sulphonate*,  $C_{47}H_{66}O_{18}Br_4S_4$ , glassy spheres, m. p.  $150^{\circ}$ ,  $[\alpha]_D + 128^{\circ}$ , and *tetrapalmitate*,  $C_{71}H_{134}O_{10}$ , needles, m. p.  $69^{\circ}$ ,  $[\alpha]_D^{18} + 46.9^{\circ}$ .

*2 : 4 : 6-Tribromophenol-d-glucoside*:—*tetra- $\alpha$ -bromocamphor- $\pi$ -sulphonate*,  $C_{52}H_{65}O_{18}Br_7S_4$ , amorphous, m. p.  $181^{\circ}$ ,  $[\alpha]_D^{20} + 75.1^{\circ}$ .

All optical data refer to solutions in chloroform.

J. K.

**Compounds of High Molecular Weight. III. Derivatives of Raffinose and of some other Sugar Derivatives of High Molecular Weight.** SVEN ODÉN (*Arkiv Kem. Min. Geol.*, 1918—1919, 7, No. 15, 23—38).—The eleven hydroxyl groups of raffinose render this compound a very suitable starting point for the synthesis of derivatives of high molecular weight. The method of acylation already described was successfully applied in this case, and gave completely acylated products (contrast Stollé, A., 1901, i, 189); but the reaction took place more slowly, and some material was always recovered unchanged; sulphonyl chlorides react still less readily than those of carboxylic acids. The products were all amorphous and definitely uniform, except possibly the hendecahexabromostearate. Amorphous derivatives were also obtained from saccharose, but mannitol and dulcitol furnished crystalline products. From inositol, only the hexa-*p*-bromobenzoate could be obtained. The following derivatives are described.



*Raffinose*:—*hendecabenzoate*,  $C_{95}H_{76}O_{27}$ , m. p.  $113^{\circ}$ ,  $[\alpha]_D^{20.5} + 106.8^{\circ}$ , *hendeca-p-chlorobenzoate*,  $C_{95}H_{65}O_{27}Cl_{11}$ , m. p.  $130-132^{\circ}$ , *hendeca-p-bromobenzoate*,  $C_{95}H_{65}O_{27}Br_{11}$ , m. p.  $136-138^{\circ}$ ,  $[\alpha]_D^{20.5} + 85.2^{\circ}$ , *hendecapalmitate*,  $C_{194}H_{362}O_{27}$ , m. p.  $53^{\circ}$ ,  $[\alpha]_D^{20.5} + 31.8^{\circ}$ , *hendecastearate*,  $C_{216}H_{406}O_{27}$ , m. p.  $62^{\circ}$ ,  $[\alpha]_D^{20.5} + 28.3^{\circ}$ , *hendecacerotate*,  $C_{304}H_{582}O_{27}$ , m. p.  $68^{\circ}$ , *hendecahexabromostearate*,  $C_{216}H_{340}O_{27}Br_{66}$ , m. p.  $147-148^{\circ}$ ,  $[\alpha]_D$  ca.  $+12^{\circ}$ , and *hendecanaphthalenesulphonate*,  $C_{128}H_{98}O_{38}S_{11}$ , m. p. ca.  $126^{\circ}$ .

*Sucrose*:—*octacinnamate*,  $C_{84}H_{70}O_{19}$ , m. p.  $87-88^{\circ}$ ,  $[\alpha]_D^{18} + 12.5^{\circ}$ , and *octa-p-bromobenzoate*,  $C_{68}H_{46}O_{19}Br_8$ , m. p.  $116-118^{\circ}$ ,  $[\alpha]_D + 27^{\circ}$ .

*Dulcitol*:—*hexa-p-chlorobenzoate*,  $C_{48}H_{32}O_{12}Cl_6$ , m. p.  $238^{\circ}$ , and *hexapalmitate*,  $C_{102}H_{194}O_{12}$ , m. p.  $74^{\circ}$ , both optically inactive.

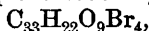
*d-Mannitol*:—*hexa-p-bromobenzoate*,  $C_{48}H_{32}O_{12}Br_6$ , prisms, m. p.  $96^{\circ}$ ,  $[\alpha]_D^{18} + 29.6^{\circ}$ .

*Inositol*:—*hexa-p-bromobenzoate*,  $C_{48}H_{30}O_{12}Br_6$ , prisms, m. p.  $264^{\circ}$ , optically inactive.

All optical data refer to solutions in chloroform.

J. K.

**Diastereomeric Acyl Derivatives of some Sugars.** SVEN ODÉN (*Arkiv Kem. Min. Geol.*, 1918—1919, 7, No. 16, 1—16).—The acylation of *d*-glucose by treatment with acid chlorides and quinoline required some days for completion at temperatures of  $30-70^{\circ}$ . In all cases, the product, corresponding in its sparing solubility in alcohol with those obtained in other instances (see preceding abstracts), was accompanied by an isomeride, easily soluble in alcohol, and differing in m. p. and specific rotation. The less soluble modifications were also obtained as sole products by the acylation of  $\beta$ -*d*-glucose, usually at rather higher temperatures, and are therefore to be derived from  $\beta$ -*d*-glucose, whilst the more soluble forms correspond with  $\alpha$ -*d*-glucose. Similar results were obtained with *d*-galactose and *l*-arabinose. In these cases, the author designates the parent sugar, of which only one solid form is known, and that modification of the acylated sugar which is analogous in respect of melting point, specific rotation, and solubility. The following compounds are described: *penta-anisoyl-d-glucose*,  $C_{40}H_{42}O_{16}$ ,  $\alpha$ -form, m. p.  $98^{\circ}$ ,  $[\alpha]_D^{19.8} + 103^{\circ}$ , and the  $\beta$ -form, amorphous, m. p.  $175^{\circ}$ ,  $[\alpha]_D^{20} + 11^{\circ}$ ; *penta-p-nitrobenzoyl-d-glucose*,  $C_{41}H_{27}O_{21}N_5$ ,  $\alpha$ -form, m. p.  $235^{\circ}$  (decomp.),  $[\alpha]_D^{19} + 176^{\circ}$ , soluble in chloroform, and the  $\beta$ -form, m. p. ca.  $265^{\circ}$  (decomp.), insoluble in chloroform; *penta-p-bromobenzoyl-d-glucose*,  $C_{41}H_{27}O_{11}Br_5$ ,  $\alpha$ -form, crystals, m. p.  $197^{\circ}$ ,  $[\alpha]_D + 110^{\circ}$ , and the  $\beta$ -form, amorphous, m. p.  $220^{\circ}$ ,  $[\alpha]_D^{18} + 83^{\circ}$ ; *penta-p-bromobenzoyl-d-galactose*,  $C_{41}H_{27}O_{11}Br_5$ ,  $\alpha$ -form, needles, m. p.  $130^{\circ}$ ,  $[\alpha]_D + 45^{\circ}$ , and the  $\beta$ -form, prisms, m. p.  $207.5^{\circ}$ ,  $[\alpha]_D + 107^{\circ}$ ; *tetra-p-bromobenzoyl-l-arabinose*,



$\alpha$ -form, m. p.  $205^{\circ}$ ,  $[\alpha]_D^{20} + 383^{\circ}$ , and the  $\beta$ -form, m. p.  $118^{\circ}$ ,  $[\alpha]_D^{20} + 228^{\circ}$ ; *hexa-p-nitrobenzoyldulcitol*,  $C_{48}H_{32}O_{24}N_6$ , crystals, m. p.  $265-268^{\circ}$ ; *octa-p-nitrobenzoylsucrose*,  $C_{68}H_{46}O_{35}N_8$ , amorphous, m. p.  $150^{\circ}$  (decomp.); *tetra-p-nitrobenzoyl-2:4:6-tribromophenol-d-glucoside*,  $C_{40}H_{25}O_{13}N_4Br_3$ , amorphous, m. p.  $247^{\circ}$ ,  $[\alpha]_D - 39^{\circ}$ ;

and *tetrapalmityl-1-arabinose*,  $C_{69}H_{134}O_9$ , amorphous, m. p.  $69.5^\circ$ ,  $[\alpha]_D^{19} + 4^\circ$ .

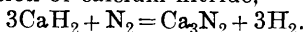
All optical data refer to solutions in chloroform. J. K.

**The Theory of Colour Lakes.** C. BRENNER (*Helv. Chim. Acta* 1920, 3, 90—103).—See this vol., ii, 194.

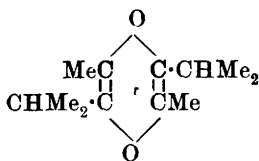
**Catalytic Reduction of Furfuraldehyde.** HANS PRINGSHEIM and HARTMUT NOTH (*Ber.*, 1920, 53, [B], 114—118).—The hydrogenation of furfuraldehyde has already been studied by Padoa and Ponti (A., 1907, i, 146), and that of furan by Bourguignon (A., 1908, i, 280). A new study of this subject has now supplied a connecting link between the earlier results. By arranging that the furfuraldehyde is exposed to the reduced nickel as much as possible, the authors have obtained furan, 1-methylfuran, and a dihydrofuran, besides the products described by Padoa and Ponti. It appears, therefore, that the hydrogenation of furfuraldehyde proceeds in three ways concurrently: (I) reduction of the aldehyde group as far as methyl, and then hydrogenation of the ring; (II) expulsion of the aldehyde group with the formation of furan, and further hydrogenation; and (III) rupture of the ring and formation of pentan- $\beta$ -ol and methyl propyl ketone. J. C. W.

**Some Reactions of Calcium Hydride.** SIGISMOND REICH and H. O. SERPEK (*Helv. Chim. Acta*, 1920, 3, 138—144).—The present investigation was undertaken on account of the importance of calcium hydride as a reducing agent, particularly in organic chemistry, and also because the data recorded by Moissan, by Erdmann and van der Smitten (A., 1908, ii, 587), and by Mayer and Altmayer (A., 1908, i, 845) are discordant in many respects.

Carbon monoxide is reduced by calcium hydride heated to dull redness, with the formation of hydrogen, methane, and formaldehyde, rather more than 16% of the carbon monoxide being converted into the latter. When a mixture of the hydride with sodium hydrogen carbonate is gently heated, formic acid is produced, the yield being 13.2% of that theoretically possible; a similar result is obtained when normal sodium carbonate is used. Ammonia is formed in small amount when nitrogen is passed over calcium hydride at about  $500^\circ$ , but the main reaction appears to consist in the formation of calcium nitride,



Acetone reacts energetically with finely divided calcium hydride, giving mesityl oxide, b. p.  $128-130^\circ$ , and the *substance* (annexed formula), b. p.  $226-236^\circ$ ; acetophenone also yields condensation products with calcium hydride at  $240^\circ$ , but these have not been fully investigated.



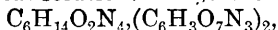
Quinoline is converted at  $220^\circ$  into  $\beta\beta$ -diquinolyl, needles, m. p.  $190^\circ$ , whilst pyridine at  $160-165^\circ$  yields a small quantity of crystalline matter,

m. p. 54—56°, which does not appear to be identical with any known dipyrindyl.

Other organic compounds, such as ethyl acetate, benzene, nitrobenzene, and anthraquinone, did not appear to react with calcium hydride under varying conditions of temperature. Calcium hydride, therefore, only appears to react as a reducing agent at very high temperatures, and its use in the hydrogenation of organic compounds must be very limited, the more so since its action, when it does occur, appears to lead preferably to condensations.

When calcium hydride is added to an ethereal solution of ferric chloride, hydrogen is evolved, and a brown precipitate is produced which is soluble in water to an acid solution; its composition is represented by the formula  $\text{Ca}_3\text{FeCl}_5(\text{C}_4\text{H}_{10}\text{O})_3$ . H. W.

**Dipicrates of Arginine and Histidine.** L. HUGOUNENQ and G. FLORENCE (*Bull. Soc. Chem. Biol.*, 1919, 1, 102—106).—The dipicrates have been prepared by the action of picric acid on the monopicrates in ethereal solution. *Arginine dipicrate*,



m. p. 156° (corr.), forms spherules of fine needles, and *histidine dipicrate*,  $\text{C}_6\text{H}_9\text{O}_2\text{N}_3(\text{C}_6\text{H}_3\text{O}_7\text{N}_3)_2 \cdot 5\text{H}_2\text{O}$ , long needles, m. p. 80°.

J. C. D.

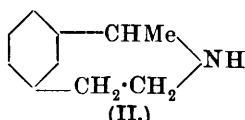
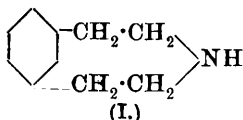
**Synthesis of some Purine Glucosides.** BURCKHARDT HELFERICH and MALTE VON KÜHLEWEIN (*Ber.*, 1920, 53, [B], 17—22. Compare Fischer and Helferich, A., 1914, i, 333).—By the interaction of the silver salts of purines with acetobromogalactose and acetobromoarabinose, followed by hydrolysis of the acetates with methyl-alcoholic ammonia, further purine-glucosides have been obtained, as follows. *Tetra-acetyltheophylline-d-galactoside*,  $\text{C}_7\text{H}_7\text{O}_9\text{N}_4 \cdot \text{C}_6\text{H}_7\text{O}_5\text{Ac}_4$ , has m. p. 135—137° (corr.),  $[\alpha]_D^{20} -13.97^\circ$ , 12.96°, in toluene, and *theophylline-d-galactoside* forms long needles, m. p. 251° (corr.; decomp.),  $[\alpha]_D^{20} +23.45^\circ$ , in water. *Tetra-acetyltheobromine-d-galactoside* crystallises in microscopic needles, m. p. 208° (decomp.),  $[\alpha]_D^{17} +9.76^\circ$ , in chloroform, and *theobromine-d-galactoside* forms minute needles with  $2\text{H}_2\text{O}$ , decomp. above 150°, and is very speedily decomposed by water. *Triacetyltheophylline-l-arabinoside* forms thin, rhombic plates, m. p. 214—216°,  $[\alpha]_D^{23} +43.34^\circ$ , in *s*-tetrachloroethane, and *theophylline-l-arabinoside* crystallises in slender needles, m. p. 276—277°,  $[\alpha]_D^{18} +34.08^\circ$ , in water. J. C. W.

**The Condensation of Ethyl Acetoacetate with *p*-Dimethylaminobenzaldehyde and Ammonia.** LEONARD ERIC HINKEL and HERBERT WILLIAM CREMER (*T.*, 1920, 117, 137—140).

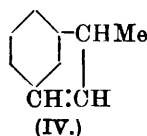
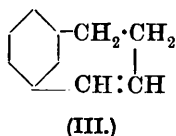
**Influence of Hydrogen-ion Concentration on the Volatility of Indole from Aqueous Solution.** HARPER F. ZOLLER (*J. Biol. Chem.*, 1920, 41, 37—44).—The range of most rapid volatilisation of indole from the aqueous solutions studied is from  $p_H$  8.0 to 10.5. This has led to the adoption of direct distillation in the separation of indole (this vol., ii, 203). J. C. D.

**Ring Closure in the Meta-position in the Benzene Series.**

**II. Reduction of *m*-Xylylene Dicyanide.** JULIUS VON BRAUN, (FRL.) L. KARPFF, and W. VON GARN (*Ber.*, 1920, **53**, [B], 98—109. Compare this vol., i, 87).—When *m*-xylylene dicyanide is reduced by means of sodium in alcohol, the normal product, the primary diamine, forms only about one-seventh of the yield. The chief product is a saturated, secondary amine of the formula (I) or (II).



It yields isophthalic acid on oxidation, and the quaternary ammonium hydroxide obtained from it after treatment with methyl iodide loses, not only water, but also dimethylamine on distillation, giving an unsaturated hydrocarbon, (III) or (IV). This may



be reduced to a saturated hydrocarbon, and both compounds yield isophthalic acid on oxidation. This result indicates, therefore, that, contrary to all experience, the two meta-carbon atoms in the benzene ring may be connected, not only by a chain containing nitrogen, but by a simple carbon chain also.

*m*-Di- $\beta$ -aminoethylbenzene,  $C_6H_4(CH_2 \cdot CH_2 \cdot NH_2)_2$ , is a colourless liquid with b. p. 165—170°/20 mm. It absorbs carbon dioxide from the air, forms a *dihydrochloride*, m. p. 290°, a *platinichloride*, m. p. 238°, and a *picrate*, m. p. 238°. Unlike the corresponding diamine of the ortho-series (A., 1917, i, 130), it reacts with methyl iodide to form a *bisquaternary iodide*,  $C_6H_4(CH_2 \cdot CH_2 \cdot NMe_3I)_2$ , m. p. 212°.

The secondary amine, (I) or (II), has b. p. 97—98°/16 mm., and forms a *hydrochloride*, m. p. 160°, a *platinichloride*, m. p. 232°, a sulphur-yellow *picrate*, m. p. 176°, a *benzoyl* derivative, leaflets, m. p. 72°, a *phenylthiocarbamide*,  $C_{10}H_{12}N \cdot CS \cdot NHPh$ , leaflets, m. p. 87°, an oily *nitroso*-compound, and a *quaternary methiodide*,  $C_{10}H_{12}NMe_3I$ , leaflets, m. p. 236° (corresponding *chloride*, and *platinichloride*,  $C_{24}H_{36}N_2Cl_6Pt$ , m. p. 228°). It also reacts with *o*-xylylene dibromide to form the compound,  $C_{10}H_{12}N \begin{smallmatrix} <CH_2 \\ | \\ CH_2 \end{smallmatrix} C_6H_4$ ,

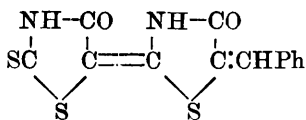
m. p. 168—169°. The unsaturated hydrocarbon, (III) or (IV), is a mobile liquid with intense, characteristic odour, b. p. 62—63°/18 mm.,  $D_4^{19}$  0.900 (unusually low compared with the isomeric hydrocarbons,  $C_{10}H_{10}$ ),  $n_D^{19}$  1.54029. It polymerises like styrene, and forms a *dibromide*, m. p. 48°. On reduction by means of colloidal

palladium, it yields the *hydrocarbon*,  $C_{10}H_{12}$ , which is a mobile liquid with pleasant odour and abnormally low density, b. p.  $50.5-51.5^\circ/14$  mm.,  $D_4^{17}$  0.852,  $n_D^{17}$  1.4968. J. C. W.

**Preparation of 3:6-Diaminoacridine.** POULENC FRÈRES and ROBERT MEYER (Brit. Pat. 137214).—*m*-Phenylenediamine is melted at  $130^\circ$  with formic acid, or oxalic acid and glycerol, or other polyhydric alcohol, and a condensing agent such as anhydrous zinc or calcium chloride; when the evolution of carbon dioxide has ceased, the temperature is raised to, and maintained for two hours at,  $150-170^\circ$ , and the diaminoacridine is isolated from the resultant, almost solid mass by treatment with water and ammonia. It may be purified through its sulphate, which is sparingly soluble in very dilute sulphuric acid. [See, further, *J. Soc. Chem. Ind.*, 1920, March.] G. F. M.

**Rhodanines.** CH. GRÄNACHER (*Helv. Chim. Acta*, 1920, 3, 152—163).—The author has attempted to elucidate the constitution of Nencki's rhodanine red, but great difficulty has been experienced in purifying the dye, since it could not be caused to crystallise; analyses of the product, moreover, show it to be more complex than was anticipated. It has, however, been shown that the imino-hydrogen of the rhodanine is not concerned with its oxidation by ferric chloride, since *N*-substituted rhodanines, such as 3-phenylrhodanine, also yield red dyes under suitable conditions. On the other hand, benzylidenerhodanine is not affected by ferric chloride, so that the presence of a free methylene group appears essential to the production of a dye.

Rhodanine appears to be tautomeric with 4-hydroxy-2-thiolthiazole, since it can be readily transformed in alkaline solution into the colourless benzoyl derivative,  $S \begin{smallmatrix} \diagup C(SBz)N \\ \diagdown CH= \\ \diagup C \end{smallmatrix} \cdot OBz$ , whilst if the methylene hydrogen atoms are substituted, as in benzylidenerhodanine, the yellow monobenzoyl derivative,  $S \begin{smallmatrix} \diagup C(SBz)=N \\ \diagdown C(:CHPh) \end{smallmatrix} \cdot CO$ , is produced. Alkylidenerhodanines react with aniline and phenylhydrazine to yield the corresponding phenylhydrazones and anilides, the sulphur of the thio-keto-group being removed as hydrogen sulphide. Since aniline is comparatively readily removed from these anilides, they can be employed for condensing the rhodanine molecule with compounds containing a reactive methylene group; in this manner, benzylidenerhodanineanilide can be condensed with a second molecule of rhodanine to yield 5-benzylidene-5'-rhodanylidene-2'-rhodanine (annexed formula). Reaction with aniline or phenylhydrazine proceeds in a totally different manner with rhodanines, such as *N*-phenylrhodanine, which contain the free methylene group; in



this case, the sulphur of the thio-keto-group remains unaffected, and complete fission of the rhodanine ring occurs, with formation of thiocarbamides or thiosemicarbazides, reaction occurring so readily that the process is conveniently used for the preparation of the latter class of substances.

The following individual substances are described: *dibenzoyl-rhodanine*, colourless needles, m. p. 126°; *5-benzylidene-2-benzoyl-mercaptothiazoline*, deep yellow leaflets, m. p. 151—152°; *5-benzylidenerhodanine-2-phenylhydrazone*, orange-red leaflets, m. p. 219° after softening at 210°; *5-p-dimethylaminobenzylidenerhodanine-2-phenylhydrazone*, red leaflets, m. p. 282° (decomp.); *5-benzylidenerhodanine-2-anilide*, pink leaflets, m. p. 252—253° after softening at 248°; *5-p-dimethylaminobenzylidenerhodanine-2-anilide*, dark yellow leaflets, m. p. 308° (hydrolysis of the two substances last named leads to the formation of 2:4-diketo-5-benzylidenethiazolidine,  $\begin{array}{c} \text{CO-S} \\ \text{NH}\cdot\text{CO} \end{array} > \text{C:CHPh}$ , m. p. 238—240°, and of 2:4-diketo-5-p-dimethylaminobenzylidenethiazolidine, long, orange-yellow needles, m. p. 296°, respectively); *5-benzylidene-5'-rhodanylidene-2-rhodanine*, brown leaflets; *diphenylthiocarbamide*, colourless leaflets, m. p. 151—152°; *diphenylthiosemicarbazide*, long, colourless needles, m. p. 176—177°. H. W.

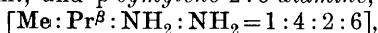
**Acyl Substituted isoThiohydantoins.** AUGUSTUS EDWARD DIXON and RAYMOND THOMAS JOACHIM KENNEDY (T., 1920, 117, 74—79).

***p*-Cymylene-2:6-diamine and the Formation of 2:4-Dinitrotoluene by the Nitration of *p*-Cymene.** J. ALFTHAN (*Ber*, 1920, 53, [B], 78—98).—With a view to the utilisation of the large quantities of *p*-cymene which accumulate in the sulphite-cellulose industry (1 kilo. per ton of cellulose), Aschan has studied the nitration of the hydrocarbon (*Finska Kemistsamfundets Meddelanden*, 1916, 25, 122). The conditions finally adopted, and now described, are the gradual addition of one part of cymene to a mixture of two parts of nitric acid (D 1.5) and four parts of sulphuric acid (1.84), the temperature being kept below 0°. The main product is a crude dinitro-derivative, which may be reduced to a crude diamine. When this is examined, it is found to consist of some 2:4-tolylenediamine, but chiefly *p*-cymylene-2:6-diamine, a new base. The occurrence of the toluene derivative therefore suggests that 2:4-dinitrotoluene is present in the nitration product, the *isopropyl* group having been expelled by a nitro-group. The mechanism of this displacement is discussed, but various probable suggestions are negatived by experience, and the question is left open. There also seems to be little hope of making the dinitrotoluene the main product, and so utilising cymene as a source of trinitrotoluene.

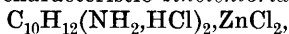
The separation of the products of nitration is a difficult matter,

distillation under reduced pressure being the best method. The crude product is partly oily and partly solid, the latter yielding 2:4-dinitrotoluene, m. p.  $70^{\circ}$ , b. p. below  $161^{\circ}/6$  mm., and 2:6-dinitro-*p*-cymene, m. p.  $54^{\circ}$ , b. p.  $161$ — $163^{\circ}/6$  mm. The oil contains, in addition, cymene, *p*-tolyl methyl ketone, and a mononitrocymene, which can be converted into the above dinitrocymene. The crude dinitro-compounds are reduced by means of tin and zinc and hydrochloric acid (tin at the commencement, zinc after the reaction has set in), and the crude diamines separated by fractional distillation under 15 mm. pressure.

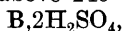
2:4-Tolylenediamine, purified by crystallisation from benzene, forms pale yellow, very hard needles, m. p.  $98$ — $99^{\circ}$ , b. p.  $160$ — $168^{\circ}/15$  mm., and *p*-cymylene-2:6-diamine,



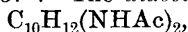
separates from 20% alcohol in glistening, thin leaflets, m. p.  $95$ — $96^{\circ}$ , b. p.  $300$ — $300.5^{\circ}/768$  mm.,  $158$ — $162^{\circ}/10$  mm., 0.7469 gram dissolving in 100 grams of water at  $25^{\circ}$ . The following salts of *p*-cymylene-2:6-diamine are described: *hydrochloride*, needles, decomp.  $180$ — $200^{\circ}$ ; characteristic *zincchloride*,



pale pink needles, decomp. above  $245^{\circ}$ ; *hydrogen sulphate*,

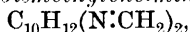


decomp.  $250^{\circ}$ ; *nitrate*, long leaflets, decomp.  $170^{\circ}$ ; *hydrogen oxalate*,  $\text{B}, 2\text{H}_2\text{C}_2\text{O}_4$ , rods, m. p.  $188$ — $189^{\circ}$  (decomp.); and *thiocyanate*, needles, m. p.  $137^{\circ}$ . The *diacetyl* derivative,

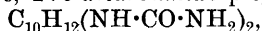


crystallises in thin needles, m. p.  $254^{\circ}$ , and yields a 3-nitro-compound, needles, m. p.  $280$ — $282^{\circ}$ , which may be hydrolysed to 3-nitro-*p*-cymylene-2:6-diamine, yellow needles, m. p.  $187^{\circ}$ . The *dibenzoyl* derivative forms needles, m. p.  $246$ — $247^{\circ}$ .

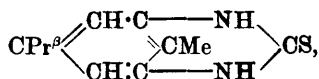
Condensation products of the cymylenediamine are as follows: with formaldehyde, 2:6-bismethyleneimino-*p*-cymene,



m. p.  $170$ — $180^{\circ}$  (decomp.); from the chloride and potassium cyanate or thiocyanate, 2:6-dicarbamido-*p*-cymene,



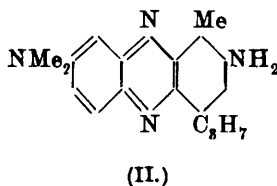
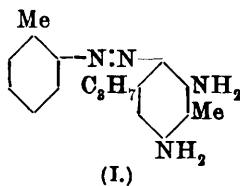
needles, m. p.  $270$ — $280^{\circ}$  (decomp.), and 2:6-dithiocarbamido-*p*-cymene, m. p.  $165$ — $175^{\circ}$  (decomp.); with carbon disulphide and alcoholic potassium hydroxide, 2-methyl-5-isopropyl-1:3-phenylene-thiocarbamide,



m. p.  $157$ — $158^{\circ}$ ; and with alcoholic oxalic acid, *m*-aminocymyloxamic acid,  $\text{NH}_2\cdot\text{C}_{10}\text{H}_{12}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , m. p.  $217$ — $218^{\circ}$  (decomp.).

The following dyes have also been prepared: a dark red *hydroxyazo*-dye,  $\text{C}_{30}\text{H}_{22}\text{O}_{14}\text{N}_4\text{S}_4\text{Na}_4$ , by diazotising at a low temperature, to avoid the production of a Bismarck-brown, and coupling with sodium  $\beta$ -naphthol-3:6-disulphonate; a *chrysoidine* of the

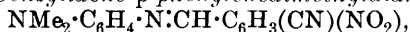
formula (I), reddish-yellow cubes, m. p. 114—115°, by coupling with diazotised *o*-toluidine; and a brownish-yellow *eurhodine*, m. p.



177—178°, of the formula (II), by condensation with *p*-nitroso-dimethylaniline.  
J. C. W.

### 2-Nitro-4-cyanobenzaldehyde and 6:6'-Dicyanoindigotin.

S. REICH and E. LENZ (*Helv. Chim. Acta*, 1920, **3**, 144—151).—2-Nitro-*p*-toluonitrile, colourless, shining needles, m. p. 107°, is prepared from 2-nitro-*p*-toluidine by a modification of the method of Niementowski and Noyes, and is converted by *p*-nitrosodimethylaniline in alcoholic solution in the presence of sodium carbonate into *p*-dimethylaminophenyl-2-nitro-4-cyanophenylazomethine [2-nitro-4-cyanobenzylidene-*p*-phenylenedimethyldiamine],



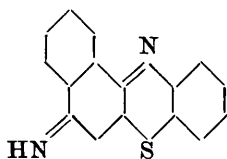
almost black needles, m. p. 182.5—183° (decomp.), which is hydrolysed by hydrochloric acid, yielding 2-nitro-4-cyanobenzaldehyde, red needles, m. p. 110°. The latter yields an *oxime*, red needles, m. p. 142—143°, and a *phenylhydrazone*, bright red crystals, m. p. 202—203° (decomp.), which could not be converted by potassium hydroxide in aqueous-alcoholic solution into an *isoindazole* derivative, a fact which is interpreted as further evidence in favour of Reich's views on the influence of the accumulation of atoms and atomic groups round the aldehydic carbon atom on such condensations (compare Reich and Nicolaeva, A., 1919, i, 171). The aldehyde, when dissolved in benzene, is converted by exposure to sunlight into 2-nitroso-4-cyanobenzoic acid, small, yellow crystals, which begin to darken at about 210°, and have m. p. 250° (decomp.). When a solution of the aldehyde in acetone is treated with dilute sodium hydroxide solution, 6:6'-dicyanoindigotin is deposited as a bluish-violet powder with metallic lustre; when heated, it does not sublime, but decomposes, with evolution of reddish-violet vapours. When reduced with sodium hyposulphite, it dyes wool and cotton from an alkaline bath in reddish-purple shades, which become blue with a tinge of violet on exposure to air, oxidation proceeding more slowly than with indigotin. The shades are fast to light and milling.  
H. W.

**Preparation of Easily Soluble Compounds of the CC-Di-alkyl-, CC-Diallyl-, and CC-Alkylaryl-barbituric Acids.** F. HOFFMANN, LA ROCHE & Co. (Brit. Pat. 122778).—Easily soluble compounds of these acids are obtained by combining them with alkylamines, for example, diethylamine or dimethylamine, by add-



ing rather more than the theoretical amount of alkylamine to the free acid, so that the latter is dissolved, and then evaporating off the excess of amine. The products are more powerful hypnotics than the free acids, and much more stable in aqueous solution than their sodium salts.

**Action of *o*-Aminothiophenol on Orthoquinones. I. 5-Imino-7:12-naphthaphenthiazine.** KNUT STAHRFOSS (*Helv. Chim. Acta*, 1920, **3**, 134—138).—*o*-Aminothiophenol hydrochloride reacts with 4-amino-1:2-naphthaquinone in boiling 80% acetic acid

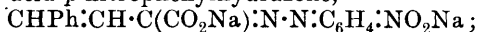


solution, with formation of 5-imino-7:12-naphthaphenthiazine hydrochloride, a chocolate-brown powder, which is stable in air and readily soluble in water. The *platinichloride* was analysed. The free base (annexed formula) is an unstable, yellow substance. The constitution of the substance follows from the conversion of the hydrochloride by concentrated sulphuric acid into a naphthaphenazthione, identical with that formed from *o*-aminothiophenol and 4-hydroxynaphthaquinone. H. W.

**New Bases for the Preparation of Mordant Dyes.** HEINRICH BAMBERGER (*Zeitsch. angew. Chem.*, 1920, **33**, i, 8).—The chlorides of *o*-nitrophenol-*p*-sulphonic acid, 6-nitro-*o*-cresol-*p*-sulphonic acid, and 6-nitrosalicyl-*p*-sulphonic acid, obtained by treatment of their potassium salts with chlorosulphonic acid, react quantitatively with aromatic amines, diamines, amino-carboxylic acids, or amino-phenols, and with amino-sulphonic acids or amino-phenolsulphonic acids of the benzene or naphthalene series. By reducing the resulting sulphamido-compounds with sodium sulphide, valuable bases are produced for mono- and bisazo-mordant dyes, which give colours ranging from yellow to bluish-violet (compare Swiss Pat. 81249—81256; Fr. Pat. 490177 [1918]). J. K.

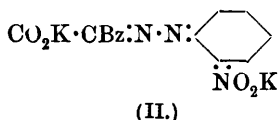
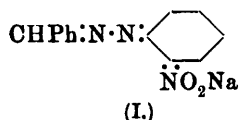
**Certain Salts with para-, ortho-, and meta-Quinonoid Structure.** R. CIUSA (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 366—371).—In contact with alkali, best in acetone solution, *p*-nitrophenylhydrazones are turned violet, addition of water to the solution or acidification yielding the initial hydrazones unchanged. That the corresponding salts, which are easily obtainable, differ in structure from the nitrohydrazones themselves is shown by their different colour in solution and by their different absorption spectrum. To explain the intense colour of these salts, the simple quinonoid constitution is insufficient, the assumption of the more complex formula,  $C_6H_4 \begin{array}{c} \text{NO}_2 \text{M} \\ \text{N} \begin{array}{c} \text{---} \text{N:CHPh} \end{array} \end{array}$ , in which the metal, M, is united by secondary valencies to the rest of the molecule, being necessary; the position at which the secondary valencies act is still uncertain. Similar complex formulæ are attributed to all the

quinonoid salts dealt with in the paper. The following salts have been prepared: the potassium salt of benzaldehyde-*p*-nitrophenylhydrazone,  $\text{CHPh}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\text{K}$ ; the disodium salt of benzylidenepyruvic acid-*p*-nitrophenylhydrazone,



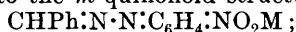
the dipotassium salt of benzoylglyoxylic acid-*p*-nitrophenylhydrazone,  $\text{CO}_2\text{K}\cdot\text{CBz}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\text{K}$ .

In alcoholic or acetone solution, *o*-nitrophenylhydrazones also dissolve in alkali, the solutions assuming a blue coloration. Crystalline salts of benzaldehyde-*o*-nitrophenylhydrazone have not been obtained, although the sodium salt (I) certainly exists in solution,



but the dipotassium salt of benzoylglyoxylic acid-*o*-nitrophenylhydrazone (II) has been prepared in shining, bronze-coloured crystals or as a blue powder.

It has been stated that benzophenone-*m*-nitrophenylhydrazone does not undergo salt formation in contact with alcoholic potassium hydroxide. The author finds, however, that a very slight change of colour does take place under these conditions, and that, in acetone solution, *m*-nitrophenylhydrazones give a green coloration with the alcoholic alkali, addition of water then resulting in the formation of the unaltered nitrophenylhydrazones. The absorption spectrum of such an alkaline solution differs from that of the original hydrazone, and persists even on dilution of the liquid. In this case, it has not been found possible to obtain crystallised salts, but it may be assumed that the salt formation occurs with change from the benzenoid to the *m*-quinonoid structure,



such *m*-quinonoid saline compounds are certainly readily hydrolysable, and the tendency to their formation small.

The experimental results are to be published elsewhere.

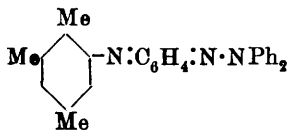
T. H. P.

**Amine-oxidation. II. Bivalent Nitrogen. Triphenylhydrazyl.** STEFAN GOLDSCHMIDT (*Ber.*, 1920, **53**, [B], 44–62).—When an ethereal solution of triphenylhydrazine (Wieland, A., 1915, i, 797) is shaken with lead peroxide, a fugitive, deep blue solution is formed which has the characteristics of solutions of compounds with bivalent nitrogen (Wieland, *ibid.*, 848). This suggests that oxidation to *hexaphenyltetrazone* has taken place, this being dissociated in solution into *triphenylhydrazyl*, thus:  $2\text{NPh}_2\cdot\text{NPh} \rightarrow \text{NPh}_2\cdot\text{NPh}\cdot\text{NPh}\cdot\text{NPh}_2 \rightarrow 2\text{NPh}_2\cdot\text{NPh}\cdots$  By carrying out the oxidation in methyl ether at  $-55^\circ$  to  $-60^\circ$ , the tetrazen may actually be isolated as a very pale green crust, which is sparingly soluble in chilled ether or light petroleum, but more soluble in toluene or chloroform. The solutions are deep blue and

do not obey Beer's dilution law, thus confirming the idea of dissociation. The dissociation depends on temperature and on the solvent. For example, ethereal solutions, which are only pale greenish-blue at  $-80^{\circ}$ , are deep blue at the ordinary temperature, and chloroform solutions are darker than ethereal solutions under the same conditions. The substance may be analysed by means of quinol, this causing reduction to triphenylhydrazine, when the liberated quinone can be titrated iodometrically.

Triphenylhydrazyl is not sensitive to oxygen, but combines with nitric oxide at low temperatures to form *N*-nitrosotriphenylhydrazine, golden prisms, m. p.  $115^{\circ}$  (Busch, A., 1907, i, 552). It also combines with triphenylmethyl, but this agent reacts too slowly to permit of the isolation of a pure product before the triphenylhydrazyl has decomposed. The decomposition of triphenylhydrazyl is accompanied by change of colour, through green to reddish-brown, the products being diphenylamine and quinoneanildiphenylhydrazone,  $\text{NPh}_2\cdot\text{N}:\text{C}_6\text{H}_4\cdot\text{NPh}$  (Wieland, A., 1911, i, 82). Ethereal solutions of triphenylhydrazine also develop the blue colour of triphenylhydrazyl on exposure to sunlight, and then yield the same decomposition products.

When a mixture of aniline and triphenylhydrazine in ether is oxidised by lead peroxide, benzoquinoneanildiphenylhydrazone is again formed. This is interpreted as the fusion of the two radicals,  $\text{NPh}_2\cdot\text{NPh} + :\text{NPh} \rightarrow \text{NPh}_2\cdot\text{N}:\text{C}_6\text{H}_4\cdot\text{NPh}$  (compare this vol., i, 226), and is confirmed by the fact that a mixture of cumidine and triphenylhydrazine gives a homologous compound (annexed formula), which crystallises in the form of its *hydrochloride* in bluish-violet, stout spikes, m. p.  $152-153^{\circ}$ . Both compounds exhibit only one absorption band, the aniline derivative at  $465-650\ \mu\mu$  and the new one at  $475-525\ \mu\mu$ . The identity of the new



compound is established by reduction to diphenylamine and *p*-aminophenylcumylamine,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_2\text{Me}_3$ , concentric groups of needles, m. p.  $86-87^{\circ}$ .

These facts are discussed in connexion with Wieland's views on the decomposition of triphenylhydrazine. It is suggested that the products are best interpreted by assuming an initial dissociation into H and  $\text{NPh}_2\cdot\text{NPh}$ .

When triphenylhydrazine is treated with ethereal hydrogen chloride at  $-20^{\circ}$ , it yields *N*-phenylbenzidine (Busch, *loc. cit.*). This is oxidised by lead peroxide in ether to *diphenoquinonephenyl-di-imine*,  $\text{NPh}:\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4:\text{NH}$ , yellowish-red needles, m. p.  $180-181^{\circ}$ .  
J. C. W.

**Hæmoglobin. I. Optical Constants.** WILLIAM H. WELKER and CHARLES SPENCER WILLIAMSON (*J. Biol. Chem.*, 1920, **41**, 75-79).—By employing the method of Marshall and Welker (A., 1913, ii, 568) for removing small amounts of other colloids from

hæmoglobin solutions, the authors were able to prepare purer specimens of crystallised hæmoglobin, which could be used for the study of the absorption coefficients of the pigment from various species. The results obtained indicate that there is not sufficient difference in the absorption coefficients of the hæmoglobin of various species to serve as a means of identification of the species. J. C. D.

**The Structure of Yeast-nucleic Acid. V. Ammonia Hydrolysis.** P. A. LEVENE (*J. Biol. Chem.*, 1920, **41**, 19—23).—The fourth nucleotide, *cytidinephosphoric acid*,  $C_9H_{14}O_8N_3P$ , m. p.  $225^\circ$  (corr.; decomp.),  $[\alpha]_D^{20} + 40-43^\circ$ , has now been obtained in a crystalline condition. There is a danger of error in assuming the existence of di- or tri-nucleotides on the basis of the results of elementary analysis, for it is shown that the free nucleotides, as well as their brucine salts, are capable of forming mixed crystals, which may furnish analytical data very nearly approaching those required by polynucleotides. J. C. D.

**Crystalline Uridinephosphoric Acid.** P. A. LEVENE (*J. Biol. Chem.*, 1920, **41**, 1—2).—The crystalline diammonium salt of uridinephosphoric acid was converted into the lead salt, which was decomposed by hydrogen sulphide. From the concentrated filtrate, the free uridinephosphoric acid,  $C_9H_{13}O_9N_2P$ , was obtained in a crystalline condition, m. p.  $202^\circ$  (corr.; decomp.),  $[\alpha]_D^{20} + 10.5^\circ$ . This research marks an important step in the chemistry of yeast-nucleic acid, as every one of the four constituent nucleotides has now been prepared in crystalline form. J. C. D.

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## Physiological Chemistry.

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**Estimation of the Alkalinity of Blood.** PEDRO J. PANDO (*Rev. Farm., Buenos-Ayres*, 1919, 167; from *J. Pharm. Chim.*, 1919, [vii], 20, 394—395).—A small flask containing 20 c.c. of water, 1 gram of 10% sodium citrate solution, and 10 c.c. of *N*/200-sulphuric acid is weighed; about 0.2 gram of blood is collected directly in the flask, which is again weighed. After the addition of 1 gram of animal charcoal, the mixture is diluted to 50 c.c., filtered, and 45 c.c. of the filtrate are titrated with *N*/200-sodium hydroxide solution, using phenolphthalein as indicator. By this method, normal blood exhibits an alkalinity equivalent to 5.50 grams of sodium hydroxide per 1000 grams. W. P. S.

**The Presence of Hæmatin in Human Blood Serum. III. Further Results from Toxicological Practice.** JOH. FEIGL (*Biochem. Zeitsch.*, 1919, 93, 119—127. Compare A., 1918, i, 241).—From observations made on munition workers, it was found that

hæmatinæmia is an important phenomenon in the course of the decomposition of blood brought about by the toxic effect of nitrous fumes ( $\text{NO}_2, \text{N}_2\text{O}_3$ ), and is more apparent than the contemporary incipient methæmoglobinæmia. Out of about thirty cases of gas poisoning (from the front), eight showed hæmatinæmia ten to twenty-eight days after the intoxication. No definite information as to the presence of hæmatin in the serum of "Röntgen gas" cases is so far available. Hæmatinæmia was absent in cases of zinc, copper, and lead poisoning. A case of arsenic hydride poisoning showed hæmatinæmia. The histories of some of the cases are given. S. S. Z.

**Antigens. XIII. The Significance of the Protein Components in the Precipitin Reaction of the Azoproteins.**

KARL LANDSTEINER (*Biochem. Zeitsch.*, 1919, **93**, 106—119. Compare A., 1918, i, 321).—Immune sera were prepared by the injection of azotised horse sera, prepared by the coupling of the serum with the diazo-compounds of aniline-*m*-sulphonic acid and *p*-arsanilic acid respectively. The precipitin reactions of the sera were then tested on various proteins azotised by means of the diazo-compounds of aniline-*m*-sulphonic acid and *p*-arsanilic acid. With the exception of gelatin and pectone, the aniline-*m*-sulphonic acid immune serum precipitated all the proteins azotised by means of the aniline-*m*-sulphonic diazo-derivative, but not the proteins azotised with the *p*-arsanilic acid derivative. The reverse happened with *p*-arsanilic acid immune serum. The author suggests that the usual immunological serum reactions do not depend on the specific chemical structure of the respective proteins, but on the dimensions of the molecule of these proteins. S. S. Z.

**Availability of Carbohydrate in certain Vegetables.**

W. H. OLMSTED (*J. Biol. Chem.*, 1920, **41**, 45—58).—Vegetables of low carbohydrate content, such as cabbage, spinach, and lettuce, are frequently employed in the diet of patients with diabetes. Estimations of the sugar-forming material in such vegetables were therefore made, either by hydrolysis of the starch with diastase, followed by estimation of the dextrose by reduction of copper solutions, or by ascertaining the extra sugar excreted by a phloridzinised dog after administration of a known amount of the vegetable. The amounts of available carbohydrate in cabbage and cauliflower, as measured by the latter method, are of the same order as those recorded in the analyses of Atwater and Bryant. The "thrice cooking" process frequently employed to remove carbohydrates from vegetables intended for consumption by diabetic patients is effective in reducing the amount of carbohydrate present by 90%.

J. C. D.

**The Influence of Alkaline and Acid Hydrolysis on the Absorption and Utilisation of Proteins. I. The Utilisation of Hydrolysed Casein.** JOHANNES MÜLLER and HANS MURSCHAUSER (*Biochem. Zeitsch.*, 1919, **93**, 34—44).—Various

hydrolysis preparations of casein were fed to a terrier, and the nitrogen metabolism was worked out in order to ascertain the amount of the protein utilised by the animal. 96.1% of the original casein was retained by the dog. The same casein, hydrolysed by shaking with 3% sodium hydroxide and heating it for one and a-quarter hours in a boiling water bath under a reflux condenser, was only utilised to the extent of 59%. When the casein was heated with 3% sodium hydroxide for two hours under a pressure of four atmospheres, 39% of the hydrolysed product was retained. The administration of opium per os to the dog fed on the alkaline product of hydrolysis of casein did not improve its retention in the organism. On the other hand, 98.6% of the casein, hydrolysed by heating it with 2.74% hydrochloric acid in a boiling water bath under a reflux condenser for four hours, was utilised. Protalbic acid, prepared by hydrolysing casein with 3% sodium hydroxide under a reflux condenser and precipitating with acetic acid, was also tried. 29% of this product was retained. S. S. Z.

**The Utilisation of Yeast in the Animal Organism.** W. VÖLTZ (*Biochem. Zeitsch.*, 1919, **93**, 101—106. Compare Schill, A., 1918, i, 359).—Living yeast, after a sojourn of six and a-half hours in the digestive tract of a dog, was excreted in the faeces in a living condition, and was capable of fermenting sugar. After remaining for nine and a-half hours inside the dog, the yeast cells were mostly dead, and about half of them were digested. The faeces in this case contained 5% of living, 20% of diseased, and 75% of dead cells. 53.3% of the total organic matter and 46.6% of the protein of the consumed yeast were utilised by the organism. It is therefore advisable to kill the yeast before utilising it for feeding purposes unless it is administered with a therapeutic object.

S. S. Z.

**Occurrence of Squalene in the Egg Oil of a Shark.** MITSUMARU TSUJIMOTO (*J. Ind. Eng. Chem.*, 1920, **12**, 73).—The oil separated from the eggs of the Japanese shark, *Lepidorhinus kinbei* (Tanaka), by extraction with ether was a light brown, semi-solid substance with an iodine value of 177.6. When treated with dry hydrogen chloride, it yielded 20% of squalene hexahydrochloride. Squalene has also been found in the egg oil of the frill shark, *Chlamydoselachus anguineus* (Garman). [See, further, *J. Soc. Chem. Ind.*, 1920, 197A.] C. A. M.

**Squalene: a Highly Unsaturated Hydrocarbon in Shark-liver Oil.** MITSUMARU TSUJIMOTO (*J. Ind. Eng. Chem.*, 1920, **12**, 63—72).—Of the numerous species of Japanese sharks, those having liver oils of low sp. gr. (below 0.9) usually have the hydrocarbon, squalene, in the oil (A., 1918, i, 89). This constituent may be approximately estimated by distilling the oil under reduced pressure in a current of carbon dioxide or other inert gas. The amount thus estimated in the liver oils of twelve species of sharks ranged

from 7.1 to 84.8%. Squalene isolated from the liver oil of the Ai-zamé shark had  $D_4^{15}$  0.8591 and  $D_4^{20}$  0.8559. Exposed to the air in a thin layer, it absorbed 13.4% of oxygen in three days and 24.0% in twenty-three days, the oxygen absorption, calculated from the formula  $C_{30}H_{50}O_6$ , being 23.66%. The dodecabromide,  $C_{30}H_{50}Br_{12}$ , when reduced with glacial acetic acid and zinc dust, yielded about 35% of an orange-yellow oil with  $n_D^{20}$  1.4950. The hexahydrochloride, when recrystallised from acetone, melted at about 125°. Its formation is the best test for the detection of as little as 1% of squalene in an oil. The hexahydrobromide forms white, lustrous crystals, turning brown at 115–118°, and melting at 125–126°, whilst the *hexahydriodide* is an unstable, white, crystalline compound, melting to a pink liquid at 108–109°. On dechlorinating the hexahydrochloride, a nearly colourless, oily liquid of  $D_4^{15}$  0.9065 was obtained. When distilled under reduced pressure, this yielded an oily distillate with iodine value 281, which appeared to be a hydroxy-derivative of squalene with the formula  $C_{30}H_{50}(OH)_2$ . It boiled at 252–254° (4.5 mm.), and had  $D_4^{15}$  0.8995 and  $n_D^{20}$  1.4938. Squalene yielded a yellow formolite, which decomposed at about 180°, but no crystalline nitrosochloride or nitrosite. On dry distillation, it yielded a small fraction, which was a hydrocarbon with molecular weight 131. Although squalene differs slightly in physical properties from the hydrocarbon, spinacene, isolated by Chapman from the liver oils of Portuguese sharks (T., 1917, 111, 56; 1918, 113, 458), it seems probable, from the similarity of the derivatives, that the two hydrocarbons are identical. [See, further, *J. Soc. Chem. Ind.*, 1920, 197A.]

C. A. M.

**Physiology of Glands. XXXVIII. The Influence of the Spleen on the Respiratory Metabolism.** NIKOLA DANOFF (*Biochem. Zeitsch.*, 1919, 93, 44–66).—The respiratory metabolism of rats was studied by means of Haldane's method. It was found that the respiratory metabolism of small animals is higher per unit body weight and time than that of larger animals, and that it rose as the surrounding temperature sank. Rats which had their spleen removed used up more oxygen and produced correspondingly more carbon dioxide than normal rats. These quantities rose from day to day soon after the operation. The respiratory quotient, however, remained the same before and after the operation. The presence of the spleen therefore reduces the respiratory metabolism, and its function in this respect is consequently opposite to that of the thyroid.

S. S. Z.

**Formation of Lactose in the Mammary Gland.** F. RÖHMANN (*Biochem. Zeitsch.*, 1919, 93, 237–253).—On digesting the extract of the mammary gland, dextrose was formed. This sugar was then converted into lævulose and galactose, and eventually into lactose. These reactions were followed up by estimating the reduction, the rotation, the formation of mucic acid by oxida-



tion with nitric acid, and the osazone formation. The degree of the dextrose formation and its transformation into the other sugars in the extract of the mammary gland are found to be influenced by the condition of the activity of the gland at the time of the animal's death. Sucrose, which was added to the extract, was also degraded by it, and the products of degradation underwent further transformation. The formation of dextrose in the extract could not be of the character of a glucoside hydrolysis, as on heating the extract with 2—10% sulphuric acid, the reduction was only increased to a small extent. This increase in reduction was shown to be due to the splitting of small quantities of lactose. The author advances the hypothesis that dextrose, which reaches the mammary gland through the blood stream, is not always utilised immediately, but is sometimes stored there as an intermediate substance, which by some still unknown fermentation process can be reconverted into dextrose. The latter, by further enzymic activity, is converted into levulose and galactose, and eventually into lactose. S. S. Z.

**The Normal Arsenic of Living Tissues and the Traces of Iodine found in the Air and in Waters. Some Necessary Corrections.** A. GAUTIER (*Compt. rend.*, 1920, 170, 261—262).

—The author reaffirms the conclusions drawn from his previous work (compare A., 1900, ii, 152, 168, 226, 670; 1903, ii, 92) as to the occurrence of arsenic in animal tissues, but draws attention to possible errors in the estimation of arsenic, due to the presence of traces of hydrogen arsenide as an impurity in the hydrogen sulphide used.

Examination of further samples of sea-water from different sources, previously found to give water containing iodine in a soluble form, now shows the complete absence of iodine in a soluble form, although minute traces of it in an insoluble form were found.

W. G.

**Carbonic Acid and Carbonates in Cows' Milk.** LUCIUS

L. VAN SLYKE and JOHN C. BAKER (*J. Biol. Chem.*, 1919, 40, 335—344).—Considerable care must be taken over the collection of the sample to ensure that there is no loss of carbon dioxide. The analysis is carried out by the method previously described for the estimation of carbon dioxide in blood plasma (Van Slyke, A., 1917, ii, 422), with one or two slight modifications, the chief of which is the employment of a 20% solution of lactic acid to disengage the carbon dioxide. With the decrease in the hydrogen-ion concentration there is a general tendency for the carbon dioxide content of milk to increase and for the degree of acidity, as measured by titration, to decrease. The results are higher than those recorded by other workers, the normal content of carbon dioxide in milk being about 10% by volume. The carbon dioxide of milk may be completely removed by exhaustion, provided the milk is spread out in a thin film and kept in motion. The removal of carbon dioxide results in a decrease in the hydrogen-ion concentration. When

milk is pasteurised, the carbon dioxide content is decreased, but the hydrogen-ion concentration is unchanged. When the carbon dioxide has been completely removed prior to pasteurisation, the hydrogen-ion concentration increases appreciably. It is suggested that the decrease of carbon dioxide in pasteurised milk might be made the basis of a method for distinguishing pasteurised from normal milk.

Carbon dioxide in milk is present as carbonic acid and as bicarbonate, probably of sodium, the ratio being about 1 to 2. The tension of carbon dioxide in milk is calculated to be about 50—55 mm. of mercury at 20° in the case of a 0.01*N*-solution with a  $p_H$  value of 6.60.

J. C. D.

**The Influence of the Acidity of the Milk on the Velocity of Inactivation of the Peroxydase by Heat.** A. BOUMA and W. VAN DAM (*Biochem. Zeitsch.*, 1918, **92**, 385—397).—The influence of the hydrogen-ion concentration on the inactivation of the peroxydase in milk at 70.55° was studied. At 70°, the  $p_H$  is two and a-half to three times higher than at the ordinary temperature. The addition of so much lactic acid to the milk as was just insufficient to curdle it on pasteurisation had no effect on the velocity constant of the inactivation of the enzyme at that temperature. On the other hand, the addition of sodium hydroxide and ammonia greatly accelerated the destruction of the peroxydase. This confirms the preliminary observations previously made by Zilva.

S. S. Z.

**The Physiological Action of the Proteinogenic Amines.**  
**I. The Influence of Proteinogenic Amines on the Nitrogen Metabolism of Dogs from which the Thyroid has been Removed.** J. ABELIN (*Biochem. Zeitsch.*, 1919, **93**, 128—149).—Phenylethylamine, *p*-hydroxyphenylethylamine, and eventually isoamylamine were administered per os to dogs from which the thyroid had previously been removed. An increase in the metabolism and greater diuresis were observed as a result of the treatment. A decrease in body weight was also recorded. As the pharmacological action of the above amines resembles that of the protein substances from the thyroid, it is suggested that the action of the thyroid on the metabolism is not due to the protein substances themselves, but to derivatives emanating from them.

S. S. Z.

**Physiological Action of Aromatic Diamines.** RICHARD MEISSNER (*Biochem. Zeitsch.*, 1919, **93**, 149—163).—*o*- and *m*-Phenylenediamines, in contradistinction to *p*-phenylenediamine, are tolerated by frogs in high doses. *o*-Phenylenediamine has also no toxic effect on rabbits. Cats, on the other hand, develop œdema typical of *p*-phenylenediamine intoxication on administration of the ortho-compound. *m*-Phenylenediamine produces no œdema in cats and rabbits, but the latter animal develops ascites. The methyl

derivatives of the above isomerides produce cerebral manifestations, and prove fatal even when given in small doses, but no œdema can be observed. The diethyl and monoacetyl derivatives, on the other hand, cause swellings in the head and neck. The insoluble diacetyl- and ethoxy-*p*-phenylenediamine are inactive. Triamino-benzene, -toluene, and -phenol produced methæmoglobinuria in cats, but not œdema. S. S. Z.

**The Pharmacology of Compounds Resembling Digitalis in their Activity.** MARGARETE WALTER (*Biochem. Zeitsch.*, 1918, **92**, 267—282).—The diffusibility, electrical charge, adsorption, and the reversibility of the action on the heart of compounds resembling digitalis in their activity were studied. No connexion between these properties could be established. S. S. Z.

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## Chemistry of Vegetable Physiology and Agriculture.

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**The Effect of Nitrogen-fixing Organisms and Nucleic Acid Derivatives on Plant Growth.** W. B. BOTTOMLEY (*Proc. Roy. Soc.*, 1920, [B], 91, 83—95).—The crude nucleic acid derivatives from bacterised peat and the growth products from *Azotobacter chroococcum* or from *Bacillus radicolica* each exert a very marked influence in increasing the growth of plants of *Lemna minor* in water culture. Not only is there an increase in the number of plants formed, but also in the weight of the plants. The crude nucleic acid derivatives, which are about as effective as the *Azotobacter* growth, are much more effective than the pure adenine-uracil dinucleotide derived from them. The joint effect of the crude nucleic acid derivatives and *Azotobacter* growth is much greater than the sum of their individual effects, being about equal to that of the water extract of an equivalent amount of bacterised peat. It is of interest to note that the crude nucleic acid derivatives, and the *Azotobacter* and *B. radicolica* growths, all give the Folin-Macallum reactions, which are stated to indicate the presence of vitamins. W. G.

**The Oxidation of Vanillin to Vanillic Acid by certain Soil Bacteria.** WILLIAM J. ROBBINS and E. C. LATHROP (*Soil Sci.*, 1919, 7, 475—485).—In solution cultures containing mineral nutrients and vanillin, the latter being the only source of carbon, and inoculated with a bacterium present in certain Alabama soils, the vanillin was first oxidised to vanillic acid, which could be isolated, but was subsequently destroyed if left in the solution. Estes's reagent, acid mercuric nitrate, gives satisfactory results in the estimation of vanillin in the presence of vanillic acid (compare A., 1917,

ii, 343), but the phenol reagent of Folin and Denis (compare A., 1912, ii, 1011) is unsatisfactory under such conditions, as vanillic acid, like vanillin, gives a blue colour with this reagent, the colour produced by the acid being much deeper than that produced by an equivalent amount of the aldehyde. The authors find that vanillic acid has m. p. 210.5—211° (corr.). W. G.

**Chemical Enzyme Studies. The Growth of Yeast in Alkaline Solutions.** HANS VON EULER and OLOF SVANBERG (*Arkiv Kem. Min. Geol.*, 1918, 7, No. 11, 1—13).—The maximum alkalinity of the medium in which a Froberg bottom yeast grew was between  $P_H=7.7$  and  $P_H=8$ . A distillery top yeast (SB II) showed decided growth\* at  $P_H=7.3$ . The maximum, however, tolerated by growing yeast depends to a great extent on the quantity of cells seeded. The maximum alkalinity for *Saccharomyces ellipsoideus* and *Pseudosaccharomyces apiculatus* was  $P_H=7.9$  and  $P_H=7.6$  respectively. The highest limit of alkalinity tolerated by *Aspergillus niger* was found to be  $P_H=9$ . S. S. Z.

**The Presence of Non-volatile Substances Possessing Aldehydic Properties in Yeast Macerations.** J. COCHIN and R. SAZERAC (*Bull. Soc. chim. Biol.*, 1914, 1, 75—77).—The authors have observed that the maceration fluids from pressed yeast give a reddish-violet colour with Schiff's reagent. The substances which give this reaction are not volatile, so that they cannot be identified with the lower aldehydes. Their exact nature has not yet been determined. J. C. D.

**Presence and Estimation of Tryptophan in Protein Material of Yeast.** PIERRE THOMAS (*Bull. Soc. chim. Biol.*, 1914, 1, 67—74).—The content of tryptophan in caseinogen is approximately 1.7 to 1.8%. The protein substance from yeast, *cérévisin*, contains about 2.3%, and is the substance containing the highest percentage of tryptophan which is known. It also contains a high percentage of lysine, a fact which places this protein in a class by itself. J. C. D.

**Invertase and Fermentation Enzymes in a Top Yeast.** HANS VON EULER and E. MOBERG (*Arkiv Kem. Min. Geol.*, 1918, 7, No. 12, 1—17).—The production and the activity of the invertase of a top yeast were only influenced to a small extent by a protoplasma poison, such as chloroform. In the top yeast investigated, it was not possible to augment the invertase by Euler's method to the extent previously done in bottom yeasts. It was further found from comparative experiments with fresh yeast that, after drying it, practically the entire invertase content was retained by the dried preparation. The amount of alcohol and carbon dioxide produced from a certain quantity of sugar in alkaline solution by dried and fresh yeast was approximately the same, and was not influenced by the addition of co-enzyme. The co-enzyme, previously heated with

sodium hydroxide, became, however, more active. The authors conclude that, besides the co-enzyme and phosphate, fermentation in alkaline solution requires another activator, most probably of the nature of an alkali salt. S. S. Z.

### **The Behaviour of certain Dyes towards Yeast-cells.**

HANS VON EULER and N. FLORELL (*Arkiv Kem. Min. Geol.*, 1919, 7, No. 18, 1—27).—Dyes are adsorbed by yeast in two ways. Some dyes penetrate the cell and are retained therein; others are adsorbed on the surface of the cell. In the former case, the cell shows the stain under the microscope; in the latter, the stain can only be detected in reflected light. The surface adsorption is the more common phenomenon of the two, and is greatly controlled by the previous preparation, especially washing, of the yeast. The adsorption in both cases is influenced by such factors as the concentration of the dye, temperature, hydrogen-ion concentration, and the presence of a fermentable sugar in the solution. The staining of yeast with chrysodine (diaminoazobenzene hydrochloride), janus-blue (safranineazo- $\beta$ -naphthol hydrochloride), ponceau 3R (sodium salt of cumidineazonaphtholdisulphonic acid), and methylene-blue impairs its fermenting capacity. S. S. Z.

### **The Culture of *Aspergillus niger* (Sterigmatocystis nigra, V. Tgh.) in Mediums in which Zinc is Replaced by Other Elements (Copper, Uranium, Vanadium).**

M. JAVILLIER (*Bull. Soc. chim. Biol.*, 1914, 1, 55—66).—*Aspergillus niger* requires, in addition to the elements carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus, potassium, silicon, magnesium, iron, and manganese provided in suitable form, a trace of zinc. The author believes that the zinc plays the rôle of a physiological catalyst, and that it is not replaceable, in the strict sense of the word, by any of the elements examined. J. C. D.

### **The Aerial Fertilisation of Plants with Carbon Dioxide.**

M. B. CUMMINGS and C. H. JONES (*Bull.*, 1919, 211, 56 pp.).—A number of plants were grown in boxes and frames in the greenhouse, the boxes having glass covers, and a current of carbon dioxide was kept constantly flowing into the enclosure. With legumes, the carbon dioxide caused an increased production of pods and beans and slightly changed the chemical composition of the plant by increasing the carbohydrate storage. With peas, the increase of seed yield was especially marked. Radishes responded only slightly, but were marketable soon, and contained a larger carbohydrate and smaller protein content. Potatoes produced more foliage and larger and better tubers when grown in an atmosphere of carbon dioxide. The stimulating effect was very marked with strawberries, and the growth of flowers was also better. In most cases where the plants were grown with carbon dioxide, a higher carbohydrate content was found and a lower protein content. Lettuce was most benefited when given 300 litres of carbon dioxide per day in boxes 130 × 70 × 30 cm.

CHEMICAL ABSTRACTS.

**The Distribution of Glycerophosphatase in Seeds.** ANTON NĚMEC (*Biochem. Zeitsch.*, 1919, **93**, 94—101).—Oil-bearing seeds show a higher content of glycerophosphatase than do leguminous seeds. The latter, however, are richer in this enzyme than the cereals. S. S. Z.

**The Change in the Character of the Nitrogen in Germinating Lupines. The Relation of the Nitrogen Titratable with Formol and the "Formalin Nitrogen" to the Total Nitrogen.** H. SERTZ (*Biochem. Zeitsch.*, 1919, **93**, 253—255).—On the addition of neutral aqueous formaldehyde to plant albumins, albuminates, and hemialbumoses, the proteins become almost insoluble. This is referred to as "formalin nitrogen." The author has determined the relation of the nitrogen in the amino-groups which combines with formol and the "formalin nitrogen" to the total nitrogen in germinated lupines at various periods of the germination. The following are the results. Before germination: formol nitrogen=12.7%, "formalin nitrogen"=86.3%. After three days' germination: formol nitrogen=18.3%, "formalin nitrogen"=82.3%. After five days: formol nitrogen 24.9%, "formalin nitrogen" 70.5%. After seven days: formol nitrogen 31.05%, "formalin nitrogen" 65.5%. After ten days: formol nitrogen 39.4%, "formalin nitrogen" 57.6%. This demonstrates the formation of soluble amino-acids at the expense of the insoluble proteins during the germination of the lupine. S. S. Z.

**Germination and Formation of Chlorophyll in a Confined Atmosphere deprived of Carbon Dioxide.** N. A. BARBIERI (*Bull. Soc. chim.*, 1919, [iv], **25**, 658—661).—A comparative study of the germination of wheat in an atmosphere deprived of carbon dioxide, in pure oxygen, and in free air, in sunlight and in the dark. All germination or commencement of germination is marked by an elimination of carbon dioxide, with the formation of chlorophyll in sunlight and of chromophyll in the dark. In an atmosphere of pure hydrogen or nitrogen there is only a slight commencement of germination. In an atmosphere of pure carbon dioxide, germination does not take place. W. G.

**The Electrometric Titration of Plant Juices.** A. R. C. HAAS (*Soil Sci.*, 1919, **7**, 487—491).—The method used was that of the gas-chain, essentially of the form described by Hildebrand (*Univ. Cal. Pub. Physiol.*, 1919, **5**, 44—69), a simplified and inexpensive type of apparatus being described. Measurements were made on soja bean tops and rhubarb stalk, and from the curves, knowing the  $P_H$  values at which various indicators change colour, it is possible to tell the amount of standard alkali required to bring the plant juice to the turning point for any indicator. The curves given show the presence of greater quantities of buffer substances in the juice of the rhubarb than in the juice of soja bean tops, the actual acidity of the rhubarb juice being much greater than that of the juice of soja bean tops. W. G.

**Hydrogen-ion Concentration of Plant Juices. I. The Accurate Determination of the Hydrogen-ion Concentration of Plant Juices by means of the Hydrogen Electrode.**

CLINTON B. CLEVINGER (*Soil Sci.*, 1919, 8, 217—226).—In the method described, a Clark electrode vessel (compare A., 1916, ii, 75) modified and adapted for work with plant juices, a simple shaking apparatus, and calomel electrodes immersed in a constant temperature water-bath are used. The apparatus is so arranged that the plant juices are saturated with hydrogen outside the electrode vessel, and only come in contact with the electrodes just prior to the readings being taken. Contact between the plant juice and the saturated potassium chloride solution is made by means of a scratch around the cock connecting the two, thus reducing the contact potential, which develops quite rapidly when the connexion is made by opening the cock wide. Duplicate measurements usually agree within 0.1 millivolt, and constant potentials are maintained for several minutes. The plant juice is prepared by macerating the tissue, wrapping it in a muslin cloth, and expressing the juice by means of a press. This gives a juice free from coarse colloidal or other material.

W. G.

**Hydrogen-ion Concentration of Plant Juices. II. Factors Affecting the Acidity or Hydrogen-ion Concentration of Plant Juices.**

CLINTON B. CLEVINGER (*Soil Sci.*, 1919, 8, 227—242. Compare preceding abstract).—In making determinations of hydrogen-ion concentration of plant juices, certain points must be noted. Expressed plant juice usually becomes more acid on keeping, whilst plants when cut and left some time before the juice is expressed usually become more alkaline. Further, it is shown that the acidity of the leaves and stems is highest in the morning and decreases during the day, whereas the acidity of the roots is highest during the day. The decreased acidity of the leaves and stems in the day is attributed to the destruction of the accumulated acids by influences such as increased light and higher temperatures.

Oats, buckwheat, soja beans, and cowpeas were grown on acid soils and on the same soils after liming, and it was found that, with the exception of buckwheat, the tops of the plants grown on the limed soil were usually more acid than the tops of those grown on the unlimed soil. The acidity of the roots of the plants appeared to be comparable with that of the soil.

Similarly, the type of fertiliser used appears to have some influence on the acidity of plants. Thus, the acidity of the tops of oats grown on unlimed soil was less than that of those grown on limed soil when sodium nitrate or ammonium nitrate was used as a source of nitrogen.

W. G.

**A Method for the Macrochemical Examination of Substances contained in Cells.** FRITZ NETOLITZKY (*Biochem. Zeitsch.*, 1919, 93, 226—230).—When the finely ground powder of *Cortex quillajae* is shaken with chloroform, a sediment, con-



sisting mostly of crystals, is deposited at the bottom. These are crystals of calcium oxalate, and contain impurities such as sand grains and cell débris. The impurities can be removed by fractional sedimentation by shaking up the deposit with chloroform, carbon tetrachloride, or bromoform. The specific gravity of the latter can be altered by the addition of alcohol or ether. By this fractional method of differential sedimentation, a powder consisting almost of pure crystals was obtained. Such purified powder showed a content of 103.7% of CaO (calculated from the formula  $\text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$ ). By titrating the oxalic acid with permanganate, 94.8% of the theoretical amount was obtained. It is suggested that "sand" impurities were responsible for the high calcium and low oxalic acid content. From the above figures, the author also concludes that the crystals from *Cortex quillajae* have the formula  $\text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$ . The calcium oxalate thus obtained was further decomposed with sulphuric acid. The liberated oxalic acid, which was recrystallised several times, was titrated with permanganate, and 99.23% of the theoretical value was recorded. The crystals obtained both from sesame seeds and *Saponaria officinalis* by sedimentation from carbon tetrachloride were too contaminated with organic matter to yield good results, but the low calcium content of the sediment is most probably also due to the higher water of crystallisation of the crystals. By this method, it is also possible to separate other substances, like aleurone grains, calcified membranes, etc., from powdered plants. S. S. Z.

**Fixation of Calcium by Calciferous Plants.** (MILLÉ) T. ROBERT (*Bull. Soc. chim. Biol.*, 1914, 1, 85—92).—Calciferous plants (les plantes calcifuges) are plants which possess a marked ability to absorb calcium. They are able to live in soil deficient in calcium by virtue of this increased power of assimilation. Another class (les végétaux calcicoles) are, on the contrary, possessed of a very low power of absorbing calcium. These require soils rich in calcium, and are able to live in the presence of an amount of calcium which would be toxic to plants of the former group.

J. C. D.

**The Distribution and Migration of Copper in the Tissues of Green Plants.** L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1920, 170, 87—93).—Copper has been shown to be present in a large number of plants and trees and in all parts of the plants. It accumulates most in the parts of the plants where there is most water and great vital activity. The parts which gradually dry up and become old gradually lose their copper, yielding it to the growing parts. The copper is thus present in a diffusible and migratory form, its migration, except in so far as amount is concerned, being comparable with that of mineral nutrients, such as potassium. The juice of all the plant organs contains copper, sometimes in comparatively large amount, sometimes only in very small amount. W. G.

**Mode of Occurrence of Hydrogen Cyanide in Plants.**

L. ROSENTHALER (*Schweiz. Apoth. Zeit.*, 1919, 57, 571—576. Compare this vol., i, 130).—The author destroys disturbing enzymes by 2% silver nitrate, or, preferably, 5% mercuric chloride solution, which also fixes hydrogen cyanide if present as such. Mercuric cyanide is formed, and is dissolved by potassium iodide in slight excess; hydrogen cyanide is then liberated by carbon dioxide.

The mercuric chloride method differentiates only between hydrogen cyanide in glucosidal (for example, amygdalin) and non-glucosidal (loose) combination (for example,  $\text{Ph}\cdot\text{CO}_2\text{H}\cdot\text{HCN}$ ), but not between the latter and free hydrogen cyanide. The silver nitrate method might do so, since silver nitrate does not at once decompose the compound,  $\text{Ph}\cdot\text{CO}_2\text{H}\cdot\text{HCN}$ . Even boiling 5% mercuric chloride solution does not liberate hydrogen cyanide from amygdalin.

Hydrogen cyanide is stated to occur only combined as glucoside in bitter almonds, cherry, laurel leaves, linseed sprouts, peach leaves, *Sorghum vulgare* leaves, and the seeds of *Phaseolus lunatus*. The occurrence of hydrogen cyanide in non-glucosidal form in the buds of cherry laurel and the young leaves of *Sambucus niger* was proved by the mercuric chloride method. The leaves of *Pangium edule* and of *Alocasia macrorrhiza* probably also contain hydrogen cyanide in similar loose combination. The occurrence of free hydrogen cyanide in plants has not been observed. CHEMICAL ABSTRACTS.

**Distribution and Migration of Mineral Salts in an Annual Plant.**

G. ANDRÉ (*Bull. Soc. chim.*, 1919, [iv], 25, 610—613).—A study of the distribution of the ash and its components in the different parts of the tall sunflower (*Helianthus annuus*) at the stage of maturity. The roots and stem contain a very small proportion of the total ash, and what is present is poor in phosphates and sulphates and rich in potassium. The leaves contain practically one half of the total ash content of the plant. This portion of the ash is very rich in lime, and comparatively so in magnesia, but very poor in potassium. The capitule contains a low percentage of ash, which is rich in phosphates and potash. The seeds contain about one-tenth of the total ash of the plant, and this portion of the ash is extremely rich in phosphates. Of the nitrogen content of the plant, about one-half is to be found in the seeds, one-quarter in the leaves, and one-eighth in the capitule. It is only in the seeds that the ash contains a higher percentage of magnesia than of lime. W. G.

**Constituents of the Leaves of *Helinus ovatus*.** JOHN AUGUSTUS GOODSON (*T.*, 1920, 117, 140—144).

**The Inversion of Sucrose during the Preservation of Oranges.** G. ANDRÉ (*Compt. rend.*, 1920, 170, 126—128).—The amount of sucrose undergoing inversion during four months in the half of an orange kept in presence of an antiseptic appar-

ently bears no relationship to the acidity of the orange expressed in terms of citric acid. Further, the actual inversion is much less than that occurring in an aqueous solution of sucrose, dextrose, and citric acid, and at about the same concentrations as in orange juice kept for seventy-eight days at the ordinary temperature. Accepting Marlinand's views as to the absence of sucrose in orange juice (compare A., 1907, ii, 644), the explanation offered is that the mixture of sucrose and citric acid is not homogeneous in the orange, the two substances being localised in different cells. W. G.

**The Inversion of Sucrose in Orange Juice.** G. ANDRÉ (*Compt. rend.*, 1920, 170, 292—295. Compare preceding abstract).—The hydrolysing action of the citric acid present in orange juice on the sucrose also present is very marked at the ordinary temperature. The action of the invertase present is also marked, but less intense than that of the citric acid. W. G.

**Properties of Plants of the Order Polygonaceæ.** A. J. STEENHAUER (*Pharm. Weekblad*, 1919, 56, 1084—1101).—The botanical structure of the leaves of many plants of the order *Polygonaceæ* is described. As regards their chemical components, no extensive research has so far been carried out, but various salts, ethereal oils, etc., have been identified in certain plants. The extraction of these from the leaves is described. Anthraquinone derivatives were found in *Polygonium convolvulus*, L., *P. dumetorum*, L., *P. Sachalinense*, Schm., *P. Sieboldii*, Hort., and possibly *P. cilinode*, Michx. For the estimation of hydroxyanthraquinone derivatives, a colorimetric method is most suitable. W. J. W.

**The Flavones of Rhus.** CHAS. E. SANDO and H. H. BARTLETT (*Amer. J. Botany*, 1918, 5, 112—119).—By the isolation of flavone pigments from *Rhus typhina*, *R. glabra*, and *R. copallina*, the authors have been able to verify the conclusions of Perkin that the same flavone is not likely to be found in both the wood and leaves of the same species. Fisetin is distinctly a wood flavone, and appears to be an end-product of metabolism. It is now known to be present in *R. cotinus*, *R. rhodanthema*, *R. typhina*, and *R. glabra*. The first two species do not belong to *Rhus* in the restricted sense, but to the genera *Cotinus* and *Rhodospheera* respectively. The authors' studies are therefore the first to demonstrate the presence of fisetin in wood of species belonging to *Rhus* proper (the true sumacs). The distinctive leaf flavone, probably a plastic substance, of *Rhus* proper is myricetin. It has been obtained from *R. Coriaria*, and the authors have been able to detect it in *R. glabra* and *R. copallina*. The authors have not been able to trace its relationship to the fisetin of the stem or to the anthocyanins of the leaves and berries. Methods of extracting fisetin and myricetin are fully described. Colour reactions and physical properties of both flavones are given, together with analytical data for the acetyl derivatives and the purified flavones.

CHEMICAL ABSTRACTS.

**Colour Changes of Sugar-cane Juice and the Nature of Cane Tannin.** F. W. ZERBAN (*J. Ind. Eng. Chem.*, 1919, **11**, 1034—1036).—The polyphenol present in sugar-cane juice, which gives a green coloration with ferric salts, and, together with oxydases and iron salts, is responsible for colour changes in the juice, is not catechol, but a true tannin derived therefrom. When heated alone, it produces catechol, but no pyrogallol; dilute acids give rise to a phlobaphen and protocatechuic acid, whilst fusion with potassium hydroxide yields protocatechuic and acetic acids, but neither gallic acid nor phloroglucinol. J. H. L.

**Identification of Citric Acid in the Tomato.** R. E. KREMERS and J. A. HALL (*J. Biol. Chem.*, 1920, **41**, 15—17).—The presence of citric acid in tomato juice has been confirmed by the isolation of its triphenacyl ester. J. C. D.

**The Effect of Hydrogen Cyanide on Plants.** C. WEHMER (*Biochem. Zeitsch.*, 1918, **92**, 364—376).—Green cress is killed within ten days by 0.24 mg. of hydrogen cyanide per 1 litre of air. In order to achieve the same effect with seeds placed in water, 71.3 mg. of the acid per litre of air are required, although 2.375 mg. of the poison per litre of air greatly impair their germination and development. Green leaves submerged in water are also killed by very dilute solutions of hydrocyanic acid. S. S. Z.

**The Influence of Arsenious Acid on Growing Tissues.** RUDOLF COBET (*Biochem. Zeitsch.*, 1919, **98**, 294—314).—The influence of arsenious acid on various plants and lower animals was studied. In the plants, no improvement in the growth was observed by the application of arsenious acid. Concentrations of 1/200,000 were found to be very toxic. Frogs' spawn and tadpoles were not so susceptible to the toxic effect of arsenious acid, but neither improvement nor retardation in growth of these organisms could be traced to the influence of the arsenic compound. S. S. Z.

**Enzymes. I. Amylase of Germinated Barley.** D. MAESTRINI (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 393—394).—A highly active amylase solution may be obtained by extracting germinated barley with water containing 0.003 mol. % of acetic acid for at least six hours. [See, further, *J. Soc. Chem. Ind.*, 1920, March.] T. H. P.

**Enzymes. II. Protease and Lipase of Germinated Barley.** D. MAESTRINI (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 456—458).—The protease and lipase of germinated barley are not extractable by water, being found, not in the filtrate, but only in the residual emulsion. If distilled water is used for the extraction, the emulsion shows no proteolytic, and but slight lipolytic, activity; if, however, the water contains 0.003 mol. % of acetic acid, the emulsion exhibits

both activities to a marked extent. [See, further, *J. Soc. Chem. Ind.*, 1920, March.] T. H. P.

**Fat-soluble Vitamine. III. The Comparative Nutritive Value of White and Yellow Maize.** H. STEENBOCK and P. W. BOUTWELL [with the co-operation of E. G. GROSS and MARIANA T. SELL (*J. Biol. Chem.*, 1920, **41**, 81—96)].—The occurrence of yellow pigment and the growth-promoting property attributed to the presence of the fat-soluble vitamine seem to be intimately associated in the maize kernel. J. C. D.

**Activity of Soil Acids.** R. E. STEPHENSON (*Soil Sci.*, 1919, **8**, 41—59).—Using a modification of Tacke's method, previously described (*ibid.*, 1918, **6**, 33), an endeavour has been made to arrive at the degree of activity of the soil acids, the lime requirements being determined by allowing different times of contact for the soil and calcium carbonate. It is shown that the more reactive acids, which are capable of giving a toxic hydrogen-ion concentration, react rather quickly, but that some soils contain a large reserve of activity, which may be described as potential rather than active, but which is, however, capable of slowly decomposing carbonates. Rather highly buffered solutions react rapidly with calcium carbonate, even in the presence of soil, thus indicating that even the more active fractions of the soil acids may be considerably buffered. So far as tested, protein materials and amino-acids, previous to decomposition in the soil, do not react readily with carbonates. The author considers that the total potential acidity of a soil, as commonly determined, does not give sufficient information. It is necessary also to know something of the activity of the acids. It is not the capacity of a soil to decompose calcium carbonate, but rather the intensity of decomposition which is most highly significant.

In a discussion on the origin of soil acidity, the development of an acid condition in soils is considered from three points of view, namely, mineral acids, organic acids, and colloids. The weathering of rocks tends to give acid alumino-silicates and silicic acids, resulting in a comparatively large reserve of slowly reactive acids. Toxic acid reactions are, however, more probably due to the presence of more soluble and highly ionised acids, such as sulphuric, hydrochloric, or nitric acids, generally introduced by the application of fertilisers. It is only occasionally, and in highly organic, badly drained soils, that organic acids accumulate to a detrimental extent; in fact, in some soils organic matter may quite likely depress the more active acidity by buffering and by supplying a base in the form of ammonia and its derivatives. W. G.

**Hysteresis of Aqueous Solutions of Humus Earth.** HEINRICH PUCHNER (*Kolloid Zeitsch.*, 1919, **25**, 196—207).—An examination of peat shows that a clear, dark yellow solution may be obtained by digesting it with cold water. During the solution,

a faintly acid, somewhat aromatic odour is noticeable. The solution obtained has an acid reaction, and, on keeping for several days, deposits a slimy, brown substance, and the clear solution then becomes alkaline. The deposit from the solution obtained from 50 grams of peat amounts to 0.490 gram, and, on incinerating this, a residue of 0.218 gram is obtained. The ignited residue contained alumina, ferric oxide, manganese oxide, lime, magnesia and alkalis, sulphate, silicate, and phosphate. The solution and the deposit were examined microscopically immediately after preparation and after measured intervals, and it is shown that, after keeping for some time, changes occurred in them, notably the formation of crystals. The clear solution after sedimentation is shown to contain gels of alumina, ferric hydroxide, and silicic acid. Microphotographs of the various preparations are reproduced in the paper.

J. F. S.

**The Carbonation of Burnt Lime in Soils.** WALTER HOGE MACINTIRE (*Soil Sci.*, 1919, 7, 325—453).—A detailed study of the rate and manner of carbonation of calcium oxide and hydroxide, as such, or when mixed with soil under various conditions.

Dry calcium oxide or hydroxide does not react with dry carbon dioxide, but a very small amount of water suffices to start the action. The ignition of calcium hydroxide gives an oxide which, in small quantities, carbonates more rapidly when exposed to moist air than does the original hydroxide. The formation of carbonate from the hydroxide is controlled by the amount of free water available to convert the calcium hydroxide from solid to solution phase. The conversion of calcium oxide to the carbonate must be preceded by the formation of the hydroxide and its solution, but when moist carbon dioxide is present the two actions are so rapid as to be considered as simultaneous. The carbonation of calcium hydroxide in atmospheric exposure tends to be checked after a time by the formation of a protecting film-coating of carbonate round included nuclei of the hydroxide.

The general conclusions to be drawn from the extensive pot and field trials are as follows: Calcium oxide or hydroxide when applied at the rate of 2—4 tons per acre will revert to the carbonate more rapidly when left on the soil surface than when mixed with a dry mulch or the moist soil, the reversion being most rapid during humid atmospheric conditions. If a dressing of the oxide or hydroxide is left on the surface for several days prior to incorporation with the soil, the treatment is in effect equivalent to an application of finely divided calcium carbonate. If the oxide or hydroxide is incorporated with the top layer of soil, prior to a more thorough dissemination throughout the soil, the concentration may be sufficient to effect a temporary, partial sterilisation in this layer, which may have beneficial results. The first action of the calcium oxide applied to the soil is with the atmospheric and soil moisture, and there is no indication, when this is completed, of any tendency

to cause chemical disintegration of soil organic matter. Neither calcium oxide nor hydroxide, when applied in the amounts commonly used in practice, can be considered as chemically destructive of soil organic matter. [See, further, *J. Soc. Chem. Ind.*, 1920, 124A.] W. G.

**Calcium Cyanamide and Dicyanodiamide as Vegetation Factors.** EDUARD LINTER (*Inaug. Diss.*, 1917; from *Bied. Zentr.*, 1919, 48, 414—417).—In contact with sand or clay in presence of carbon dioxide, dicyanodiamide solution undergoes no change, but humous soils are able to absorb the dicyanodiamide with avidity, the poisonous effect on vegetation gradually disappearing. [See also *J. Soc. Chem. Ind.*, 1920, 166A.] T. H. P.

**Prevention of Volatilisation of Ammonia by means of Calcium Chloride.** A. STUTZER (*Fühling's Landw. Zeit.*, 1919, 68, 59—63).—Five grams of a sulphate or chloride of an alkali or alkaline earth metal were boiled for fifteen minutes with 250 c.c. of ammonium carbonate solution containing 0.25 gram of nitrogen; the percentage of ammonia which was volatilised was 77 with potassium, sodium, or calcium sulphate, 80 with magnesium sulphate, 87 with potassium chloride, 88 with sodium chloride, 83 with magnesium chloride, and 17 with calcium chloride. Five % of the ammonia volatilised from a solution of ammonium chloride which was exposed with calcium carbonate to the air for twelve days. The addition of 2 parts, 4 parts, and 6 parts of calcium chloride to 1 part of a volatile ammonium salt prevents 25, 50, and 75%, respectively, of the ammonia from volatilising; to preserve 90% or more of the ammonia, 8 parts of calcium chloride must be added for 1 part of nitrogen. Good results are secured when 6 parts of calcium chloride, which is a better conserving medium than gypsum, are added to urine for every 1 part of nitrogen.

CHEMICAL ABSTRACTS.

**Guano from Sardinia.** M. GIUA (*Gazzetta*, 1919, 49, ii, 246—249).—The author has analysed a number of samples of bat guano from the Borutta grotto at Sassari, Sardinia. Streaks or veins of a white, friable material, greasy to the touch, occur in the guano, particularly in that of recent origin; this consists of tricalcium phosphate, together with calcium carbonate, silica, oxides of iron, aluminium and magnesium, and small proportions of nitrates, and resembles ordinary phosphorite, being formed by the action on the calcium carbonate of the surrounding rock either of the phosphoric acid present in freshly formed guano or of ammonium phosphate. The occurrence of this material in the guano is regarded as confirmation of the view that many phosphatic deposits owe their origin to deposits of guano. T. H. P.

## Organic Chemistry.

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**Low Temperature Carbonisation.** FRANZ FISCHER and W. GLUUD (*Ber.*, 1920, **53**, [B], 250—251).—The authors maintain their scientific and technical priority (compare A., 1919, i, 377) against Tern (this vol., i, 1). H. W.

**The Interaction of Chlorine and Marsh Gas under the Influence of Light. The Conversion of Methyl Chloride into Methyl Alcohol and Methyl Acetate.** JOHN REGINALD HARVEY WHISTON (*T.*, 1920, **117**, 183—190).

**Derivatives of Pentanes from Petroleum and certain of their Homologues.** OSSIAN ASCHAN (*Öfvers. Finska Vet. Soc.*, 1915, **58**, pp. 122; from *Chem. Zentr.*, 1918, ii, 939—941).—An account is given of the action of chlorine on the paraffins and of other substances prepared from the chloro-derivatives. The chief products investigated are the pentane mixture, b. p. 30—38°, a hexane, and a fraction, b. p. 10—12°, obtained during distillation of the pentanes. Starting from isopentane,  $\text{CHMe}_2\text{Et}$ , it has been found possible to synthesise completely the main constituents of fusel oil, namely, the two primary isoamyl alcohols, isobutylcarbinol and sec.-butylcarbinol, which can thus be prepared cheaply and in unlimited quantity, since isopentane occurs abundantly in all known mineral oils. The application of isopentane and other suitable hydrocarbons from mineral oils (*n*-butane, *n*-pentane, and various hexanes, particularly  $\beta\gamma$ -dimethylbutane) to the preparation of isoprene and its homologues has been investigated. It is found that all the isopentyl chlorides, certain of them therefore under isomerisation, lose hydrogen chloride under suitable conditions, with the formation of  $\beta$ -methyl- $\Delta^2$ -butylene; the latter unites with chlorine in definite circumstances to yield the corresponding dichloride, which is converted by the action of bases into isoprene. It is also found that the dichloroisopentanes, obtained by direct chlorination of the hydrocarbon, and probably containing  $\beta$ -methyl- $\Delta^2$ -butylene chloride, lose hydrogen chloride at a sufficiently high temperature and yield isoprene.

**I. Derivatives of isoPentane.**—Dry chlorination of isopentane yields a mixture of the four isopentyl chlorides, together with dichlorides, which are interesting on account of their relationship to isoprene.  $\delta$ -Chloro- $\beta$ -methylbutane has b. p. 99—102°,  $D_{15}^{25}$  0.8692;  $\alpha$ -chloro- $\beta$ -methylbutane, b. p. 96—99°,  $D_{15}^{25}$  0.8818;  $\gamma$ -chloro- $\beta$ -methylbutane, b. p. 90—93°,  $D_{15}^{25}$  0.8752;  $\beta$ -chloro- $\beta$ -methylbutane, b. p. 85.5—88°,  $D_{15}^{25}$  0.8692.  $\beta$ -Methylbutyl acetate, prepared from the corresponding isoamyl chloride, potassium acetate, and acetic acid at 190—200°, has b. p. 140—142°,  $D_{15}^{25}$  0.8720, and, on hydrolysis, gives the corresponding isoamyl alcohol, b. p. 128.5—129.5°/



772 mm.  $\delta$ -Methylbutyl acetate has b. p. 139—142°, and is converted by alcoholic potassium hydroxide into  $\gamma$ -methylbutyl alcohol, b. p. 130—133°. The constitution of the alcohols is decided by oxidising them to the corresponding valeric acids.  $\beta$ -Methyl- $\Delta^{\beta}$ -butylene (in addition to very little acetate) is the main product of the action of potassium acetate on *sec.*-isoamyl chloride and the sole product obtained from *tert.*-isoamyl chloride. For purposes of comparison, the latter was prepared by the action of hydrogen chloride on methylbutylene in anhydrous ether; it was found to be the sole product of the change, and to be entirely reconverted into methylbutylene by removal of hydrogen chloride. Attempts are described to obtain the isopentyl acetates by the use of alcoholic potassium acetate, and it is found that the isoamyl chloride from fusel oil (containing much primary isoamyl chloride and little primary active isoamyl chloride, and therefore consisting of the most difficultly decomposed isopentyl chlorides) is converted at 200° completely into amyl acetate and amyl alcohol. Moist chlorination of isopentane leads to the production of small quantities of *sec.*-isoamyl chloride, large amounts of primary isoamyl chloride and primary active isoamyl chloride, and no *tert.*-isoamyl chloride. The best yields of monochloropentanes are obtained from light petroleum when it is subjected to dry chlorination, and it is found that *n*-pentane is less easily acted on than is isopentane. The mixture of monochlorides obtained from isopentane behaves towards alcohol and potassium acetate in the same manner as isopentyl chloride from fusel oil. isoPentyl chloride does not react with 2% potassium hydroxide solution at 60—70°. Only slight transformation occurs when isoamyl chloride is heated at 250°, more marked, but still incomplete, change at the same temperature in the presence of concentrated hydrochloric acid. Further chlorination of *tert.*-isoamyl chloride gives  $\beta$ -methyl- $\Delta^{\beta}$ -butylene chloride in unsatisfactory yield; the product which is thus obtained, as also the dichloride prepared by the direct chlorination of isopentane, yields isoprene when heated with reagents which remove hydrogen chloride at 300—400°.

When the vapours of fermentation amyl alcohol are led over aluminium hydroxide impregnated with finely divided copper and heated at dull redness,  $\beta$ -methyl- $\Delta^{\beta}$ -butylene is mainly formed. Regulated chlorination of the latter gives mainly isoamylen chloride,  $\text{CH}_2\text{:CMe}\cdot\text{CHMeCl}$ , and but little dichloride; probably a second chloroamylen, possibly  $\text{CMe}_2\text{Cl}\cdot\text{CH:CH}_2$ , is also formed. The fraction, b. p. 90—100°, and the dichloride can be used in the preparation of isoprene. Different products are obtained when hydrogen bromide is removed from methylbutylene bromide by different bases. Elimination of both bromine atoms only occurs incompletely;  $\beta$ -bromo- $\gamma$ -methyl- $\Delta^{\alpha}$ -butylene is obtained in the pure condition by the use of alcoholic potassium hydroxide. Unsuccessful attempts are described to prepare the corresponding glycol by the oxidation of  $\beta$ -methyl- $\Delta^{\beta}$ -butylene with potassium permanganate.

The author describes experiments on the distillation of caoutchouc and on the conversion of isoprene obtained by heating the vapour of turpentine oil into its derivatives. The process first named yields only 1.9% of crude isoprene and 13% of a hydrocarbon (? terpene), b. p. 170—175°, which has not been more closely investigated. Pyrogenic decomposition of turpentine gives about 5% of crude isoprene, b. p. 30—40°; in the fraction b. p. up to 100°, at least two further hydrocarbons are found, one of which, b. p. ca 70°, occurs in particularly large amount and is unstable towards permanganate; the fractions of higher b. p. contain undecomposed terpenes, benzene, and its simpler homologues. The crude isoprene is purified by conversion into  $\beta\delta$ -dibromo- $\beta$ -methylbutane, b. p. 67°/9 mm., from which it is regenerated by potassium hydroxide; the pure isoprene has b. p. 34—34.5°/758 mm.,  $D_{15}^{20}$  0.6848,  $D_4^{20}$  0.6811,  $n_D^{20}$  1.41540. Experiments are also described on the conversion of technical crude isoprene into already known isoprene derivatives. It is found that not only amylene, but also all hydrocarbons which contain at least one true ethylenic linking, can be condensed with isoprene by means of aluminium chloride to yield similar condensation products. Conversely, hydrocarbons other than isoprene, which contain two conjugated double bonds, can be condensed with amylene and other singly unsaturated hydrocarbons. Variation of the relative amount of amylene and isoprene causes variation in the composition of the products. The author claims to have discovered the condensing action of sodium on isoprene independently of, and simultaneously with, Harries and Matthews; he obtained from crude isoprene and sodium a product, insoluble in alcohol but soluble in ether, which he terms "semicaoutchouc," which can be vulcanised. Sodium has no action on pure  $\beta$ -methyl- $\Delta^2$ -butylene. Pure isoprene, when heated alone during thirteen days, was less completely polymerised than after three days in the presence of sodium. Experiments on polymerisation by metallic oxides and on vulcanisation of semicaoutchouc are also described.

II. *Experiments with n-Pentane from Petroleum.*—A second *n*-pentyl chloride, b. p. 96—98°, is formed in addition to the previously described  $\alpha$ -chloropentane, b. p. 106.6°, by the chlorination of *n*-pentane obtained from petroleum; an isopentane derivative is not produced.

III. *Examination of Petroleum Fraction*, b. p. 10—12°.—When the fraction is chlorinated in the presence of water, the main product is a chloride,  $C_4H_7Cl$ , b. p. 69—70°, thus showing that it consists mainly of a butane; the presence of isobutane could be definitely established, but *n*-butane appears either to be absent or present in small quantity. The b. p. of isobutane has been given as -17°, but this can scarcely be correct. It is remarkable that, whilst the naturally occurring fatty acids have a normal carbon chain, the hydrocarbons obtained from petroleum have, in general, branched chains.

IV *Certain Hexane Derivatives from Petroleum.*—Preliminary

experiments on the chlorination of a hexane fraction, b. p. 58—60°, and consisting chiefly of diisopropyl, led to the identification of both the possible monochloro-derivatives of this hydrocarbon, together with a third monochlorohexane, the constitution of which has not been elucidated. H. W.

**Oxidation of Hydrocarbons by Oxygen.** **Oxidation of Paraffin.** C. KELBER (*Ber.*, 1920, **53**, [B], 66—71).—Paraffin, vaselin, petroleums, and the higher fatty acids may be rapidly oxidised by submitting them to the action of finely divided streams of oxygen at 140—150°, especially in the presence of manganese compounds. In the case of a paraffin with m. p. 50—51°, 25% of the product was a distillate, consisting of oil and aqueous solution, in which acetone, formic, acetic, propionic, butyric, valeric, hexoic, octoic, nonoic, and decoic acids were identified. The pasty residue contained 40—50% of fatty acids insoluble in water, but soluble in light petroleum, and 5—10% of acids insoluble in petroleum.

J. C. W.

**Nitration of Ethylene.** HEINRICH WIELAND and EUKLID SAKELLARIOS (*Ber.*, 1920, **53**, [B], 201—210).—The hypothesis has been advanced by Thiele and elaborated by Holleman that substitution in the benzene series is preceded by addition, and that the primary reaction is similar in the ethylene and benzene series; in the former case the additive products, however, are stable, whilst in the latter, rearrangement immediately occurs, with the production of a more stable system. A certain amount of experimental evidence is available in the instances of halogenation and sulphonation, but very little work has been done on the nitration of ethylenic substances. The authors have therefore studied the behaviour of ethylene towards nitrating acid, and have shown that, under suitable conditions, ethylene dinitrate and nitroethyl nitrate are produced; it would thus appear that reaction is primarily additive in character, and results in the formation of  $\beta$ -nitroethyl alcohol, which, under the experimental conditions, is further esterified.

Ethylene is passed through an ice-cold mixture of nitric acid (D 1.4) and concentrated sulphuric acid containing 20% of sulphur trioxide, and the products are separated by distillation with steam and subsequent careful fractionation under diminished pressure; ethylene dinitrate, colourless oil, b. p. 105.5°/19 mm., D<sup>17</sup> 1.433, and  $\beta$ -nitroethyl nitrate, colourless, poisonous oil, b. p. 120—122°/17 mm., D<sup>18</sup> 1.468, are thus isolated. The latter is converted by phosphoric oxide into nitroethylene (compare A., 1919, i, 307).

Discrepancies between the properties of specimens of  $\beta$ -nitroethyl alcohol obtained by the authors and those described by V. Meyer and Henry have led them to examine in greater detail the action of silver nitrite on ethylene iodohydrin; it is found that the substance which is thus prepared is contaminated with ethylene glycol mononitrite, which can be removed by careful fractionation, and

with ethylene glycol, which cannot be thus removed, but is readily eliminated by washing the product with water. Pure  $\beta$ -nitroethyl alcohol is a colourless, odourless liquid, b. p.  $103^{\circ}/11.5$  mm.,  $D_{13.3}^{20}$  1.309; it is miscible in all proportions with water, alcohol, and ether. The aqueous solution does not give a coloration with ferric chloride, and the ketonic form can only be detected for a few seconds with this reagent after cautious acidification of the sodium salt. Contrary to Henry's observations, it cannot be distilled at the ordinary pressure, since it is thereby decomposed into water and nitroethylene.

Attempts to isolate nitroacetaldehyde in substance have not been successful up to the present; if, however, a mixture of  $\beta$ -nitroethyl alcohol and sulphuric acid is added to a boiling suspension of lead peroxide in water and the distillate is treated with *o*-nitrophenylhydrazine hydrochloride, *nitroacetaldehyde-o-nitrophenylhydrazone*, slender, orange-red needles, m. p.  $83.5^{\circ}$ , is obtained.

H. W.

**Preparation of Propylene.** ARTHUR HEINEMANN (D.R.-P. 315747; from *Chem. Zentr.*, 1920, ii. 186).—Acetylene is caused to unite with methane in the presence of contact substances consisting of mixtures of noble metals (platinum, iridium, and palladium) and common metals (iron, nickel, copper, silver, aluminium). The technical preparation of the contact agent is effected by depositing the common metal, such as copper, either electrolytically or by purely chemical reduction of a copper salt on a porous material, such as pumice; the latter is placed in a solution of a noble metal (for example, platinous chloride), dried, and, if necessary, again reduced. Methane is completely utilised at  $100$ – $200^{\circ}$  if an excess of acetylene is employed. The heating may be replaced by the chemically active violet or ultra-violet rays, or by the silent electric discharge. The yield of propylene is 70% of that theoretically possible.

H. W.

### **The Action of Nitric Acid on Unsaturated Hydrocarbons.**

**The Action of Nitric Acid on Acetylene.** KENNEDY JOSEPH PREVITÉ ORTON and (MISS) PHYLLIS VIOLET MCKIE (T., 1920, 117, 283–296).

**Preparation of Methyl Chloride and Bromide from Methyl Sulphate.** CH. BOULIN and L. J. SIMON (*Compt. rend.*, 1920, 170, 595–597).—Methyl chloride may readily be prepared in a very pure state and with an excellent yield by allowing methyl sulphate to drop into hydrochloric acid ( $D$  1.112) at about  $50^{\circ}$ , the change occurring being represented by  $\text{Me}_2\text{SO}_4 + \text{HCl} = \text{MeHSO}_4 + \text{MeCl}$ . The hydrochloric acid may be replaced by a concentrated solution of sodium chloride, but in this case a slightly higher temperature is necessary.

In the same way, methyl bromide may be obtained by letting

methyl sulphate drop into hydrobromic acid at 45—50°, or, preferably, into a concentrated solution of an alkali bromide, slightly acidified with sulphuric acid, at 30—35°. W. G.

**Organic Chemical Reagents. V. The Preparation of Alkyl and Alkylene Bromides.** OLIVER KAMM and C. S. MARVEL (*J. Amer. Chem. Soc.*, 1920, **42**, 299—309).—A detailed study has been made of the preparation of *n*-butyl bromide from the corresponding alcohol by the hydrobromic acid method; addition of sulphuric acid to the reaction mixture was found to be of more value than an increase in the quantity of hydrobromic acid. The effectiveness of sulphuric acid does not depend entirely on the resulting removal of water from the reaction mixture, but is also to be explained by the formation of an alkyl hydrogen sulphate, which probably reacts more readily with hydrobromic acid; the effect of sulphuric acid in preventing the distillation of alcohol from the reaction mixture is also an important factor.

The Norris-Bodroux method for the preparation of primary alkyl bromides has been modified in the following manner. The alcohol is treated with a 25% excess of aqueous hydrobromic acid, together with sulphuric acid. The mixture is heated under reflux in order to convert the alcohol as completely as possible into the corresponding bromide, and the latter is then removed from the reaction mixture by direct distillation. Slight variations from this procedure depend on the physical and chemical properties of the alcohol used or of the bromide formed in the reaction. For example, in the preparation of ethyl and allyl bromides, the mixture is not heated under reflux, because of the volatility of the former compound and the chemical reactivity of the latter; in the preparation of *iso*amyl bromide, a somewhat smaller proportion of sulphuric acid is used in order to prevent charring; haloids of high molecular weight, because of their high boiling points, are separated from the reaction mixture mechanically instead of by distillation. Detailed directions are given for the preparation of the following compounds, the corresponding yields being enclosed within brackets: *n*-butyl bromide, b. p. 101—104° (95—97%); *iso*amyl bromide, b. p. 116—120° (88—90%); trimethylene bromide, b. p. 162—165° (88—95%); trimethylene chlorobromide, b. p. 142—145° (89%); ethyl bromide, b. p. 38—40° (90—95%); allyl bromide, b. p. 69—72° (92—96%); *n*-octyl bromide, b. p. 196—200° (91%); lauryl bromide, b. p. 175—180°/45 mm. (91%).

The requisite hydrobromic acid solution is conveniently prepared by the reduction of bromine by sulphur dioxide in the presence of water; the mixture may be utilised directly without a preliminary distillation, the necessary additional quantity of sulphuric acid being added as concentrated acid.

Mixtures of constant boiling hydrochloric and hydrobromic acids, such as are obtained when alkyl bromides are used with aluminium chloride in Friedel-Crafts' reactions, may be separated readily by fractional distillation. H. W.

**Gaseous Methyl Fluoride. I. Revision of the Atomic Weight of Fluorine.** E. MOLES and T. BATURCAS (*J. Chim. Phys.*, 1919, **17**, 537—588).—The methyl fluoride was prepared either by heating together methyl potassium sulphate and potassium fluoride or by passing the vapour of methyl iodide over anhydrous silver fluoride at 90°. The weight of a normal litre of methyl fluoride was found to be 1.5454 grams, whilst measurements made at 506.67 mm. and 253.33 mm. indicate that the departure from Avogadro's law is given by  $1 + \lambda = 1.0181$ , and the coefficient of compressibility of methyl fluoride is 0.000037 per mm. The weight of a normal litre of oxygen under similar conditions was 1.4293, hence the molecular weight of methyl fluoride is 34.021 and the atomic weight of fluorine is 18.998.

Measurements of the vapour pressure of methyl fluoride between  $-77^\circ$  and  $-105^\circ$  give as its b. p.  $-78.2^\circ/760$  mm. The molecular heat of vaporisation, calculated by the Clausius-Clapeyron formula, is  $\lambda = 4361$  cal., and from this the Ramsay-Trouton constant is found to be 22.4. The critical temperature deduced by the Guldberg-Guye rule is  $T_c = 325.3^\circ$ .

In the preparation of methyl fluoride by the action of methyl iodide on silver fluoride, a brick-red compound is formed, which has the composition  $2\text{AgF}, \text{AgI}$ . W. G.

**The Dehydrogenation of Primary and Secondary Alcohols by Catalytic Oxidation. General Method of Preparation of Aldehydes and Ketones.** CHARLES MOUREU and GEORGES MIGNONAC (*Compt. rend.*, 1920, **170**, 258—261).—Finely divided silver, deposited on asbestos by precipitation from silver nitrate with formaldehyde, is an excellent catalyst for the oxidation of primary and secondary alcohols to aldehydes and ketones respectively. The vapour of the alcohol, mixed with slightly less than the theoretical amount of air, is passed over the catalyst heated at 230—300°. In some cases the action is so intense as to cause very marked local rise in temperature of the catalyst, and consequent destruction of some of the products of oxidation. In this case, it is better to conduct the operation in two stages. First pass the alcohol vapour, mixed with 40—50% of the requisite amount of air, over the catalyst, and then mix the issuing vapours with the other 50% of air and pass the new mixture over a second lot of the catalyst. Good results were obtained with methyl, ethyl, butyl, amyl, allyl, benzyl, cinnamyl, isopropyl, and secondary butyl alcohols by this method. W. G.

**Organic Chemical Reagents. VI. Reagents from *n*-Butyl Alcohol.** ROGER ADAMS and C. S. MARVEL (*J. Amer. Chem. Soc.*, 1920, **42**, 310—320).—The discovery of the method by which starch may be fermented to give acetone and *n*-butyl alcohol has caused the latter substance to become available in large quantity at a low price. The authors show it to be a valuable material for the preparation of *n*-amyl derivatives and *n*-hexoic

acid and its derivatives. Detailed instructions are given for the preparation of the following substances, the yields being placed within brackets: *n*-butyl bromide (this vol., i, 282); *n*-butyl cyanide, b. p. 138—141°, from the bromide and sodium cyanide in aqueous-alcoholic solution (75—80%); *n*-valeric acid, b. p. 183—186°, from butyl bromide and sodium cyanide, and hydrolysis of the crude product with sodium hydroxide (81%); ethyl *n*-valerate, b. p. 142—146°, from *n*-butyl cyanide, ethyl alcohol, and sulphuric acid (85—90%); *n*-amylamine, b. p. 102—105°, by addition of a solution of *n*-butyl cyanide in alcohol to a suspension of sodium in toluene (57—68%); *n*-amyl alcohol, by reduction of ethyl *n*-valerate by sodium in the presence of alcohol (56—61%); ethyl *n*-butylmalonate, b. p. 144—145°/40 mm., 235—240°/ordinary pressure, from *n*-butyl bromide and ethyl sodiomalonate (89—92%); *n*-hexoic acid, b. p. 200—205°, by hydrolysis of ethyl *n*-butylmalonate with potassium hydroxide, acidification of the solution with hydrochloric acid, and subsequent distillation (74%);  $\alpha$ -bromohexoic acid, b. p. 148—153°/30 mm., by bromination of *n*-butylmalonic acid and elimination of carbon dioxide from the product (71%);  $\alpha$ -aminohexoic acid, from the  $\alpha$ -bromo-acid and ammonia (65%).

H. W.

### Synthesis of Tertiary $\alpha$ -Keto-alcohols: Correction.

D. GAUTHIER (*Compt. rend.*, 1920, **170**, 325).—It has previously been indicated that cyanohydrins of the type  $\text{HO}\cdot\text{CR}^1\text{R}^2\cdot\text{CN}$  react with organo-magnesium haloids,  $\text{R}^3\text{MgX}$ , to give  $\alpha$ -ketonic tertiary alcohols,  $\text{HO}\cdot\text{CR}^1\text{R}^2\cdot\text{COR}^3$  (compare A., 1911, i, 513). It has since been found that the main product of such a reaction is the tertiary alcohol,  $\text{CR}^1\text{R}^2\text{R}^3\cdot\text{OH}$ . Consequently, the substance previously described as acetyldimethylcarbinol,  $\text{CH}_3\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{OH}$ , is really trimethylcarbinol, and the two substances described as propionyl-dimethylcarbinol,  $\text{C}_2\text{H}_5\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{OH}$ , and acetylmethylethylcarbinol,  $\text{CH}_3\cdot\text{CO}\cdot\text{CMeEt}\cdot\text{OH}$ , are really dimethylethylcarbinol.

W. G.

### Catalytic Preparation of Ethers in the Dry Way. A.

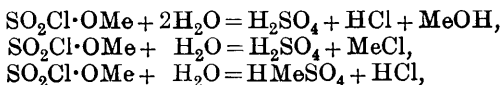
MAILHE and F. DE GONON (*Bull. Soc. chim.*, 1920, [iv], **27**, 121—126; *Compt. rend.*, 1920, **170**, 329—331).—Using the method previously described for the catalytic preparation of ethyl ether (this vol., i, 6), calcined alum being the catalyst, the authors have succeeded in preparing a number of simple and mixed aliphatic ethers from the corresponding alcohols up to *iso*amyl alcohol. *iso*Propyl alcohol and *isobutyl* alcohol only gave very small yields of the corresponding ethers.

W. G.

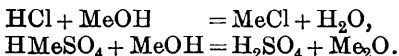
### Action of Water on Methyl Chlorosulphonate. J. GUYOT

and L. J. SIMON (*Compt. rend.*, 1920, **170**, 326—328).—The action of water on methyl chlorosulphonate depends on the relative

amounts of water and sulphonate present. The action is complex and is regulated by three changes, thus:



with which, under some conditions, are joined the actions:



The primary change is the one which produces methyl hydrogen sulphate, which is, in its turn, decomposed by an excess of water to give sulphuric acid and methyl alcohol. The latter change is limited by the reverse action, but for a large excess of water the proportion of methyl hydrogen sulphate remaining is small and independent of the amount of water.

When the amount of water diminishes, the concentration of the acids becomes important, the esterification of the methyl alcohol becomes of main importance, and consequently a more and more marked synthetic production of methyl chloride occurs. W. G.

**Action of Water on Methyl Sulphate.** CH. BOULIN and L. J. SIMON (*Compt. rend.*, 1920, 170, 392—394).—If a large excess of water acts on methyl sulphate for a relatively short time, a unimolecular reaction occurs, thus:  $\text{Me}_2\text{SO}_4 + \text{H}_2\text{O} = \text{MeHSO}_4 + \text{MeOH}$ .

If the proportion of sulphate to water is 1:10, at the end of twenty-four hours a second action is noticeable,  $\text{Me}_2\text{SO}_4 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{Me}_2\text{O}$ , and this action becomes preponderant. At the same time, a secondary change may occur,  $\text{Me}_2\text{SO}_4 + \text{MeOH} = \text{MeHSO}_4 + \text{Me}_2\text{O}$ .

Methyl sulphate is, however, soluble in water at 18° to the extent of 28 grams per litre, this solubility being modified by the accumulation of the sulphuric acid and methyl ether resulting from the above changes. W. G.

**The Sulphochromic Combustion of Methyl Esters.** J. GUYOT and L. J. SIMON (*Compt. rend.*, 1920, 170, 514—516).—The esters were oxidised by chromic anhydride in the presence of sulphuric acid, the carbon dioxide liberated being collected in a Bunte burette and measured. In some cases, the reacting mixture required heating in a water-bath. Satisfactory results were obtained with all the esters tried. The change apparently takes place in two stages, methyl hydrogen sulphate being first formed,  $\text{R}\cdot\text{CO}_2\text{Me} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{R}\cdot\text{CO}_2\text{H} + \text{MeHSO}_4$ , and oxidation then occurring.

Under similar conditions, ethyl esters undergo little or no oxidation, except in those cases where the organic acid radicle is readily oxidised, in which case ethyl hydrogen sulphate is formed and the organic acid is oxidised.



Substituted radicles, whether methyl or ethyl, do not undergo oxidation at all readily. Thus, methyl malonate is readily oxidised, but with methyl methylmalonate the oxidation is very incomplete.

W. G.

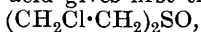
**$\beta\beta'$ -Dichloroethyl Sulphide.** CHARLES STANLEY GIBSON and (SIR) WILLIAM JACKSON POPE (T., 1920, 117, 271—278).

**A Synthesis of  $\beta\beta'$ -Dichlorodiethyl Sulphide (Mustard Gas).** J. E. MYERS and H. STEPHEN (*J. Soc. Chem. Ind.*, 1920, 39, 65T).—By passing pure ethylene into cooled sulphur dichloride until no further absorption takes place, a product containing 65% of mustard gas with 20—25% of sulphur monochloride is obtained. The formation of the latter compound, together with the evolution of considerable quantities of hydrogen chloride, is probably due to the decomposition of sulphur dichloride into the monochloride and chlorine, which then chlorinates the mustard gas. This secondary reaction is best avoided by spraying the dichloride (a mixture of 75% dichloride and 25% monochloride being most suitable) by means of compressed ethylene into an atmosphere of ethylene. In this manner, a product containing 93% mustard gas is obtained.

A solution of sodium hypochlorite containing sodium hydrogen carbonate was found to remove mustard gas almost immediately from the surface of shells.

J. K.

**$\beta\beta'$ -Dichloroethyl Sulphide.** P. SPICA (*Gazzetta*, 1919, 49, ii, 299—302; *Boll. chim. farm.*, 1919, 58, 361—363).—The author has prepared  $\beta\beta'$ -dichloroethyl sulphide by a method which is not described, but is simpler than that originally used by V. Meyer. This compound forms long, silky, white needles, m. p. 10—11°, b. p. 180—185°/20—25 cm., 215—217° (decomp.); in the liquid state it has  $D_{15}^{25} 1.275$ , and is colourless, its odour recalling that of garlic. It is an oxidisable compound, and on this property depends the use of calcium hypochlorite, potassium permanganate, etc., to neutralise its effects. Concentrated nitric acid acts slowly on it and yields varying results, but the action of 30% hydrogen peroxide solution in glacial acetic acid gives first the sulphoxide,



m. p. 50—52°, which acts as an irritant on the eyes and skin, especially when vaporised from solution, and afterwards the sulphone,  $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{SO}_2$ , m. p. 110°, which is almost non-volatile in a current of steam and exerts no irritating action.

Of the various reagents proposed for the detection of  $\beta\beta'$ -dichloroethyl sulphide, the only one which is specific is sodium iodide, this giving the corresponding di-iodo-compound. The presence of vapour of the sulphide in the air may also be detected by the formation of the sulphone occurring when the air is passed through a glacial acetic acid solution of hydrogen peroxide (see above), and also by the white turbidity, due to the formation of Meyer's non-

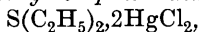
resolvable diethylene disulphide, produced when the air is passed through a narrow tube into hot sodium sulphide solution.

T. H. P.

### Synthetical Experiments with $\beta\beta'$ -Dichloroethyl Sulphide.

WILLIAM DAVIES (T., 1920, 117, 297—308).

**isoAmylsulphonium Compounds.** RUDOLF WEGSCHEIDER and HELENE SCHREINER (*Monatsh.*, 1919, 40, 325—339).—Only a slight quantity of sulphonium compound was produced by the interaction of isoamyl iodide with diisoamyl sulphide for five months. This was not due to steric influences, since, although the velocities of combination of the sulphide with methyl, ethyl, and isoamyl iodides diminish in the order given, that of the sulphide with ethyl iodide is much greater than in the case of ethyl sulphide and isoamyl iodide. As the equation,  $SR^1R^2 + R^3I = SR^1R^2R^3I$ , shows, the speed of the reaction is primarily determined by the mobility of the halogen atom (compare Carrara, A., 1895, ii, 8; Strömholm, A., 1900, i, 325). In conformity with this explanation, isoamyl iodide cannot be prepared from the corresponding chloride in the same manner as can benzyl iodide (Späth, A., 1914, i, 1). Double salts of triisoamylsulphonium iodide with zinc, cadmium, and mercuric iodides can, however, easily be prepared by warming mixtures of isoamyl iodide and sulphide with the metallic iodide at 100°. *Bistriisoamylsulphine zinc-iodide*,  $2S(C_5H_{11})_3I \cdot ZnI_2$ , has m. p. 134°; the corresponding *cadmi-iodide*,  $2S(C_5H_{11})_3I \cdot CdI_2$ , forms yellow needles, m. p. 126—127°, and is decomposed by hot water; the *dimercuri-iodide*,  $3S(C_5H_{11})_3I \cdot 2HgI_2$ , forms light yellow crystals, m. p. 66—67° to a turbid liquid, becoming clear at a somewhat higher temperature. An indefinite product was obtained from bismuth iodide. Triisoamylsulphonium iodide could not be liberated from its salts, but was probably produced by prolonged action of the iodide on the sulphide in presence of molecular silver. *Diethyl sulphide dimercurichloride*,



separates from alcohol in colourless crystals, m. p. 127°, which are decomposed by water.

J. K.

### Preparation of Acetic Anhydride.

FREDERICK PEACOCK LEACH and THE UNITED ALKALI Co., LTD. (Brit. Pat. 137701).—Acetic anhydride is produced by the interaction of anhydrous sodium acetate and carbonyl chloride according to the equation  $2CH_3 \cdot CO_2Na + COCl_2 = (CH_3 \cdot CO)_2O + CO_2 + 2NaCl$ . The reaction is started by suspending sodium acetate in acetic anhydride and adding alternately, with cooling, carbonyl chloride and sodium acetate, keeping the latter in slight excess, until a desired amount of the mixture has been produced. A portion of the liquor is then run off into a still, and the acetic anhydride distilled off in a vacuum, whilst fresh quantities of sodium acetate and carbonyl chloride are added to the mixture remaining in the reaction vessel.

G. F. M.

**Preparation of Aliphatic Acids by Catalytic Oxidation of Primary Alcohols.** A. MAILHE and F. DE GODON (*Compt. rend.*, 1920, 170, 517—519).—Primary aliphatic alcohols readily undergo catalytic oxidation in the presence of finely divided copper at 260—270°, giving an appreciable yield of the corresponding acids, but at the same time an important amount of the aldehyde is also formed. In the case of ethyl alcohol, the highest yield obtained was 18.18 grams of acetic acid and 12 c.c. of acetaldehyde from 100 c.c. of alcohol. W. G.

**Preparation of Aliphatic Esters.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 315021; from *Chem. Zentr.*, 1919, iv, 1104).—Acetylene is allowed to act on a molar mixture of fatty acid and alcohol in the presence of the mercury salts of mineral acids, preferably at an increased temperature. Thus, acetic acid is agitated with precipitated mercury oxide at 30—40° until complete solution is obtained, after which sulphuric acid (D 1.81) is added drop by drop, which causes the precipitation of mercuric sulphate in a finely divided condition; after addition of ethyl alcohol, the mixture is heated at 70° under reflux, and, with constant agitation, treated with acetylene. Acetaldehyde, which is formed as a by-product, is separated from ethyl acetate by fractional distillation. Ethyl formate is obtained when the acetic acid is replaced by formic acid, whilst methyl propionate is prepared from methyl alcohol and propionic acid. H. W.

**Preparation of  $\alpha$ -Sulphopropionic Acid.** H. J. BACKER and J. V. DUBSKY (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, 22, 415—416).—The general methods of Franchimont (A., 1888, 1175) and of Melsens, when applied to the preparation of  $\alpha$ -sulphopropionic acid, have the respective advantages of greater purity and better yield of the product. Both of these are conserved by a combination of the two processes, consisting in the addition of crystalline pyrosulphuric acid to propionic anhydride. An average yield of 0.75 mol. of acid per 1 mol. of anhydride is thus obtained. J. K.

**Ammonium Tetroxalate, a Product of the Decomposition of isoAmyl Nitrite.** H. SANDQVIST and E. MOHLIN (*Ber.*, 1920, 53, [B], 171—173).—A crystalline deposit, needles or rods, m. p. 129.5—130.5° (decomp.), deposited on the sides of a bottle containing commercial amyl nitrite which had become extensively decomposed, was found to consist of ammonium tetroxalate. Formation of these crystals in similar circumstances has been observed by Bödtger (A., 1916, i, 2), who, however, overlooked the nitrogen content, and considered them to be methanetetracarboxylic acid. H. W.

***l*-Hexylsuccinic Acid.** HENRY WREN and HENRY BURNS (T., 1920, 117, 266—268).

**The Resolution of Racemic Acids by Optically Active Alcohols. I. The Resolution of *r*-Tartaric Acid by *l*-Borneol.**

HENRY WREN, HOWELL WILLIAMS, and WILLIAM WHALLEY MYDDLETON (T., 1920, 117, 191—199).

**Preparation of Succinyldiacetic Esters.** RICHARD WILLSTÄTTER (D.R.-P. 300672; from *Chem. Zentr.*, 1920, ii, 338).—Neutral or faintly acid solutions of acetonedicarboxylic acid esters are submitted to electrolysis. The secondary potassium salts of acetonedicarboxylic acid ester are obtained by the action of potassium hydroxide in concentrated aqueous or in alcoholic solution on acetonedicarboxylic esters. The dipotassium salt of ethyl hydrogen acetonedicarboxylate yields, on electrolysis, *ethyl succinyldiacetate*, colourless needles, m. p. 46—47°, which with ammonia or amines yields pyrrole derivatives, for example, *1-methylpyrrolediacetic ester*, prisms, m. p. 164°. The corresponding methyl derivative of succinyldiacetic acid is formed less smoothly from methyl hydrogen acetonedicarboxylate, and is converted into *dimethyl 1-methylpyrrolediacetate*, needles, m. p. 170—171°. The succinyldiacetic ester constitutes the starting point for the synthetic preparation of derivatives of tropine. H. W.

**The Preparation of Glyoxal by the Action of Ozone on Acetylene.** A. WOHL and K. BRÄUNIG (*Chem. Zeit.*, 1920, 44, 157).—It is well known that ozone and acetylene interact with explosive violence. It has now been found that when the gases are suitably diluted and contain a certain amount of moisture, interaction proceeds smoothly, with formation of a mixture of glyoxal and formic acid. The products are obtained as an aqueous solution by spraying water into the reaction vessel. The solution contains 1.5 to 2.0% of glyoxal. A certain amount of nitric acid is formed at the same time, and this must be neutralised before the solution is evaporated, to avoid decomposition of the glyoxal. The latter can be isolated by known methods, for example, as its aniline derivative, or can be directly converted into glycollic acid or ethylene glycol. The aniline derivative, the anilide of anilinoacetic acid, can be used for the preparation of indigotin. E. H. R.

**Preparation of Monobromoacetone.** J. D. RIEDEL (D.R.-P. 298944; from *Chem. Zentr.*, 1920, ii, 337).—Solutions of bromine in bromide liquors are added to hot solutions of acetone containing bromoacetone in bromide liquors; the latter are obtained by neutralising the aqueous solutions from previous preparations. Monobromoacetone is thus obtained in good yield and in an immediately pure condition. H. W.

**Preparation of Monobromo-ketones.** J. D. RIEDEL (D.R.-P. 298953, additional to D.R.-P. 298944; from *Chem. Zentr.*, 1920, ii, 337. Compare preceding abstract).—Solutions of bromine in bromide liquors are added at an elevated temperature to solutions of the homologues of acetone (containing the bromo-ketone) or to a mixture of ketones and bromide liquors; the neutralised aqueous solutions from previous preparations are utilised as bromide liquors.

The instance of bromomethyl ethyl ketone, transparent, yellow liquid, is cited in particular. H. W.

**A New Hydrazone of some Monosaccharides (*m*-Tolylhydrazones of *l*-Arabinose, Rhamnose, Fucose, *d*-Galactose, and *d*-Mannose).** A. W. VAN DER HAAR (*Rec. trav. chim.*, 1920, **39**, 191—193).—*m*-Tolylhydrazine gives the following hydrazones: *l*-arabinose-*m*-tolylhydrazone, prismatic needles, m. p. 156—157°; *rhamnose-m*-tolylhydrazone, m. p. 134°; *fucose-m*-tolylhydrazone, microscopic needles, m. p. 165°; *d*-mannose-*m*-tolylhydrazone, amorphous; *d*-galactose-*m*-tolylhydrazone, needles, m. p. 154°. Xylose and *d*-fructose did not give such hydrazones, and the one from dextrose could not be obtained sufficiently pure. W. G.

**Oxidation of Sugars by Mercuric Acetate in the Presence of Ammonia.** T. INGVALDSEN and L. BAUMAN (*J. Biol. Chem.*, 1920, **41**, 147—148).—Ammonium gluconate and ammonium galactonate may be obtained in 50% yield by the action of mercuric acetate on dextrose or galactose in the presence of ammonia. Mannose and lactose are also oxidised by this method, but the ammonium salts of the acids formed have not been isolated in crystalline form. J. C. D.

**The Heptoses from Gulose and some of their Derivatives.** F. B. LA FORGE (*J. Biol. Chem.*, 1920, **41**, 251—256).—Gulose was converted into a mixture of  $\alpha$ - and  $\beta$ -guloheptonic acids by the cyanide synthesis. A mixture of the barium salts yielded on crystallisation rosettes of plates of the barium salt of  $\alpha$ -guloheptonic acid,  $C_{14}H_{26}O_{16}Ba$ .

$\alpha$ -*d*-Guloheptonic acid was a colourless syrup, which did not crystallise. It yielded a crystalline *phenylhydrazide*, long, white needles, m. p. 191—192° (uncorr.),  $[\alpha]_D^{20} - 15.38^\circ$ .

$\alpha$ -*d*-Guloheptose,  $C_7H_{14}O_7$ , obtained by reduction with sodium amalgam, forms rosettes of long needles, m. p. 185—187° (uncorr.),  $[\alpha]_D^{20} - 65.65^\circ$ .

$\alpha$ -Guloheptitol,  $C_7H_{16}O_7$ , rosettes of hard prisms, m. p. 138—141° (uncorr.). No rotation was shown by an approximately 5% solution in water. 1.0624 Grams in 25 c.c. of saturated borax solution gave in a 4-dcm. tube  $\alpha_D + 0.68^\circ$ .

$\beta$ -Guloheptonic acid and  $\beta$ -guloheptose were obtained from the mother liquors of the barium salt of  $\alpha$ -guloheptonic acid. On reduction of the syrupy  $\beta$ -guloheptose, another syrup was obtained, which, as it did not crystallise, was converted into *benzylidene*- $\beta$ -guloheptitol, m. p. 260° (decomp.).

$\beta$ -Guloheptitol,  $C_7H_{16}O_7$ , has m. p. 128—129° (uncorr.). 0.3175 Gram in 5 c.c. of saturated borax solution showed no appreciable rotation in a 1-dcm. tube. J. C. D.

**The Constitution of the Disaccharides. IV. The Structure of the Fructose Residue in Sucrose.** WALTER NORMAN HAWORTH (T., 1920, **117**, 199—208).

**Biochemical Synthesis of a Mannobiose.** EM. BOURQUELOT and H. HERISSEY (*J. Pharm. Chim.*, 1920, [vii], **21**, 81—85).—The enzyme seminase (A., 1900, i, 320) obtained from lucerne seeds, when kept for ten months in concentrated mannose solution containing a small quantity of toluene, converted the mannose, in part, into a sugar having a higher optical rotation. This sugar was isolated in an impure state, and appeared to be a mannobiose.  
W. P. S.

**Determination of the Value of Different Acids for the Liquefaction of Starch.** P. BETTINGER (*Bull. Assoc. Chim. Sucr.*, 1919, **37**, 126—131).—The relative activities of hydrochloric, sulphuric, and certain organic acids in producing liquefaction of the starch in ground cereals, under similar conditions of heating, are accounted for by the different degrees of ionisation of the acids. [See, further, *J. Soc. Chem. Ind.*, 1920, 244A.] J. H. L.

**Action of Saliva Ash on Starch Solution.** FR. N. SCHULZ (*Fermentforsch.*, 1919, **3**, 72—74; from *Chem. Zentr.*, 1920, i, 8—9).—In repeating Biedermann's experiments (this vol. i, 15) with saliva ash, the author has encountered the same difficulties as Wohlgemuth and Sallinger. Since the ash was strongly alkaline in reaction, whilst Biedermann describes the use of a neutral or faintly acid ash, and, on the other hand, the dependence of diastatic processes on the reaction is well known, the ash was made very faintly acid with hydrochloric acid. Reaction was immediately observed, which could be stopped by addition of an excess of the acid. The time of action varied between twenty minutes and several (generally four to six) hours. Optimum action probably depends on the absolute quantity of ash and a definite degree of acidity. Urine ash, when kept faintly acidic, invariably gives a positive result.  
H. W.

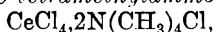
**Autolysis of Starch. Reply to Wohlgemuth and Sallinger.** W. BIEDERMANN (*Fermentforsch.*, 1919, **3**, 70—71; from *Chem. Zentr.*, 1920, i, 9. Compare this vol., i, 15).—The discordant results obtained by Wohlgemuth (A., 1919, i, 361) and Sallinger (this vol., i, 15) are explained by the different reaction of the saliva ash in the various instances. The ash used by the author was neutral or very faintly acidic; it now appears that this behaviour is exceptional, and that the hydrolysis of starch by saliva ash is dependent on the reaction of the latter, as is to be expected from the known influence of alkali on amylase action (compare Schulz, preceding abstract).  
H. W.

**Lignin. II. Fusion of the Lignosulphonic Acids with Potassium Hydroxide.** MAX HÖNIG and WALTER FUCHS (*Monatsh.*, 1919, **40**, 341—349).—The removal of the sulphonic groups from the barium salts previously described (A., 1918, i, 375) by fusion with potassium hydroxide is only complete at 250—300°. In each case, protocatechuic acid is the sole product (compare Melander,

A., 1919, i, 473) obtained after solution of the fused mass in water, acidification, filtration from insoluble matter (amounting to about one-third of the purely organic portion of the original material), and extraction with ether, the quantity obtained corresponding with 13—19% of the organic portion of the original material. In addition, a small quantity of material is not removed from the aqueous solution by ether. The lignosulphonic acids are therefore complicated aromatic sulphonic acids containing the carbon skeleton of protocatechuic acid. J. K.

**Preparation of Methylamine from Ammonium Methyl Sulphate.** WILLIAM SMITH DENHAM and LIONEL FREDERICK KNAPP (T., 1920, 117, 236—247).

**Double Salts of Cerium Tetrachloride.** F. DI STEFANO (*Annali Chim. Appl.*, 1919, 12, 130—136).—Owing to the instability of quadrivalent cerium, the tetrachloride of that metal has not been isolated, but Koppel (A., 1899, ii, 98) prepared stable double salts of cerium tetrachloride with pyridine, quinoline, and triethylamine, which he concluded to be derivatives of a hydrochloroceric acid,  $H_2CeCl_6$ . Various new double salts of this acid are now described. The *tetramethylammonium* salt,



was prepared by adding a concentrated solution of tetramethylammonium chloride in methyl alcohol to a solution of ceric chloride in the same solvent, and washing the resulting yellow, crystalline precipitate first with methyl alcohol saturated with hydrogen chloride, and then with ether. It is stable in absolutely dry air, but completely decomposed on exposure to moist air, and when dissolved in water rapidly liberates chlorine. The *tetraethylammonium* salt,  $CeCl_4 \cdot 2N(C_2H_5)_4Cl$ , is obtained in an analogous manner. It is much more stable than the preceding compound, and is only slowly decomposed when dissolved in water. It liberates iodine from potassium iodide (ratio of Ce to active Cl = 1:0.99). The *caffeine* salt,  $CeCl_4(C_8H_{10}O_2N_4 \cdot HCl)_2$ , forms reddish-orange, silky crystals which are quite stable in dry air, and only decompose slowly in moist air (ratio of Ce to active Cl = 1:1.06). Theobromine hydrochloride gave a yellow, crystalline powder with cerium tetrachloride, the exact composition of which could not be determined owing to the presence of the excess of alkaloid hydrochloride, but was probably  $CeCl_4 \cdot 2(C_7H_8O_2N_4 \cdot HCl)$ . The *quinine* salt,  $CeCl_4 \cdot 2(C_{20}H_{24}O_2N_2 \cdot 2HCl)$ , was obtained in large, reddish-orange crystals, in which the ratio of cerium to active chlorine was 1:1.

C. A. M.

**A New Method for the Preparation of Hexamethylene-tetramine.** WALTHER HERZOG (*Zeitsch. angew. Chem.*, 1920, 33, 48).—If commercial ammonium carbonate is treated with 40% formaldehyde solution, it readily dissolves, even without application of heat, with brisk evolution of carbon dioxide and formation of hexamethylenetetramine. The solution is evaporated to dryness on a

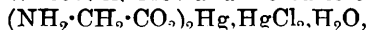
water-bath under reduced pressure, and the residue is either sublimed in a vacuum or recrystallised from absolute alcohol. The amount of ammonium carbonate should be about 10% in excess of the theoretical quantity. A yield of about 66% is obtained.

W. J. W.

**Solubility of Hexamethylenetetramine.** F. Utz (*Süddeutsch. Apoth. Zeit.*, 1919, **59**, 832; from *Chem. Zentr.*, 1920, i, 170).—1.67 Grams of hexamethylenetetramine dissolve in one part of water at the ordinary temperature (D 1.0985); larger quantities dissolve in hot water and separate on cooling the solution. At the ordinary temperature, 100 c.c. of the solvents dissolve the following amounts of hexamethylenetetramine, expressed in grams: ethyl ether, 0.06 (on warming, 0.38); trichloroethylene, 0.11; xylene, 0.14; carbon disulphide, 0.17; benzene, 0.23; tetrachloroethane, 0.50; acetone, 0.65; carbon tetrachloride, 0.85; amyl alcohol, 1.84; absolute alcohol, 2.89; 90% alcohol, 5.58 (large quantities dissolved in the hot solvent separate from the cooled solution until the latter contains 6.4 grams); methyl alcohol, 7.25 (in warm solution, 11.93). Chloroform is the best solvent, the cold solution containing 13.40 and the hot solution 14.84 grams; the bulk of the dissolved substance can be precipitated from its solution in chloroform by addition of ether. Hexamethylenetetramine is insoluble in light petroleum. When obtained from solution and dried in the steam-oven, hexamethylenetetramine is somewhat volatile with the vapour of the solvent, 18.38% of it being removed in forty hours. Determination of the refraction is best effected in aqueous methyl-alcoholic solution.

H. W.

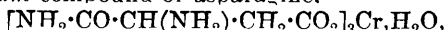
**Metallic Compounds of Glycine and Asparagine. II.** A. BERNARDI (*Gazzetta*, 1919, **49**, ii, 318—325. Compare A., 1914, i, 1167).—The double compound of mercury aminoacetate (compare Ley and Kissel, A., 1899, ii, 485) and mercuric chloride,



prepared from glycine and mercuric chloride in dilute alcohol at 50—60°, forms a white, infusible precipitate, which gradually loses its water of crystallisation in the air.

The double compound of mercury asparagine and mercuric sulphate,  $[\text{NH}_2\cdot\text{CO}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}_2]_2\text{Hg}\cdot\text{HgSO}_4$ , forms a white, flocculent precipitate and decomposes, without melting, at a high temperature; it is rapidly decomposed in the hot by concentrated potassium hydroxide solution and by ammonia solution, with precipitation of mercury in the former case and of mercuriammonium sulphate in the latter.

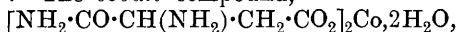
The chromium compound of asparagine,



prepared from asparagine and chromic acetate, crystallises in tufts of amaranth-red needles, forms an alkaline aqueous solution, and decomposes at about 200°. The nickel compound of asparagine,  $[\text{NH}_2\cdot\text{CO}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}_2]_2\text{Ni}\cdot 2\text{H}_2\text{O}$ , prepared from asparagine and nickel hydroxide, crystallises in blue, rectangular plates, has



an alkaline reaction in boiling aqueous solution, and decomposes at above 200°. The *cobalt* compound,

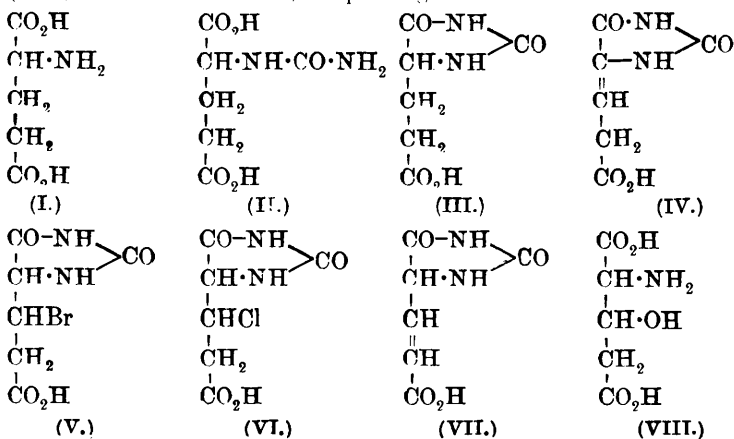


prepared from asparagine and cobalt hydroxide, crystallises in amaranth-red mamillary masses, shows an alkaline reaction in boiling aqueous solution, and decomposes at above 200°.

T. H. P.

**Amino-acids. II. Hydroxyglutamic Acid.** HENRY DRYSDALE DAKIN (*Biochem. J.*, 1919, **13**, 398—429).—The author has described previously the isolation of  $\beta$ -hydroxyglutamic acid from the products of hydrolysis of caseinogen (A., 1919, i, 150).

Attempts to synthesise this acid by brominating the acetyl derivative of  $\beta$ -hydroxyglutaric anhydride, and then acting on the bromo-compound with ammonia or by reducing ethyl  $\alpha$ -oximinoacetonedicarboxylate, were unsuccessful. Small traces of a substance closely resembling the desired amino-acid were obtained, after some difficulty, by reducing with sodium amalgam the condensation product of orthoformic ester and ethyl oximinoacetonedicarboxylate, and a similar result was obtained by the application of Strecker's method to malic semialdehyde. More satisfactory results were obtained with glutamic acid (I), which was converted into  $\alpha$ -carbamidoglutamic acid (II) by the action of potassium cyanate, and hydantoinpropionic acid (III) was obtained from the carbamido-acid by the action of hydrochloric acid. The action of bromine on hydantoinpropionic acid in concentrated solutions in glacial acetic acid gave two products. One would appear to be hydantoin- $\beta$ -bromopropionic acid (V) and the other hydantoin- $\beta\gamma$ -propenylic acid. If the action of bromine is carried out in presence of fuming hydrochloric acid, hydantoin- $\beta$ -chloropropionic acid (VI) is obtained. The conversion of hydantoin- $\beta$ -bromopropionic acid into the desired hydroxyglutamic acid was not accomplished with ease. On boiling with water, an unsaturated acid (VII) is obtained, which, on prolonged treatment with hot barium



hydroxide solution, is converted into  $\beta$ -hydroxyglutamic acid (VIII). Calculated on the original glutamic acid, the yield is about 2%.

Sufficiently large amounts of the new amino-acid were not obtained to permit of a detailed study, but its properties are all similar to those of the naturally occurring acid isolated from caseinogen. It gives a cherry-red colour with diazobenzene-sulphonic acid in the presence of sodium hydroxide, which becomes intensely deep on warming.

Other methods of synthesis were attempted, but were not found practicable. Such were bromination of benzoylglutamic acid, with the hope of obtaining benzoylaminoglutamic acid by removal of hydrobromic acid; reduction of *o*-toluidineazoacetonedicarboxylic ester, and of various hydrazine derivatives of that ester; condensation of oxymethylenehippuric ester with malonic ester; condensation of dichloroacetal with malonic ester, followed by reactions analogous to Leuch's synthesis of serine; reduction of oximinoglutamic ester and of ethyl hydroxyisooxazolidedicarboxylate.

The following compounds are described: *Hydantoin- $\beta$ -bromopropionic acid*,  $C_6H_7O_4N_2Br$  (V), white cubes and rhombic prisms, m. p. 228—230° (decomp.). *Hydantoin- $\beta$ -propenyllic acid*,  $C_5H_6O_4N_2$  (IV), sulphur-yellow, hexagonal prisms, m. p. 222—223°, solid sublimate being obtained. *Hydantoin- $\beta$ -chloropropionic acid*,  $C_5H_7O_4N_2Cl$ , rectangular plates. *Hydantoinacrylic acid* (VII),  $C_6H_6O_4N_2$ , rosettes of sulphur-yellow needles, m. p. 256—258° (decomp.).  $\beta$ -Hydroxyglutamic acid (VIII),  $C_5H_8O_5N$ , passes, on heating, into hydroxypyrrolidonecarboxylic acid. Copper salt, very soluble in water, insoluble in alcohol. *Strychnine salt*,  $C_{26}H_{31}O_7N_3$ , rosettes of needles. Malic semialdehyde, or  $\beta$ -hydroxy- $\gamma$ -aldehydobutyric acid,  $C_4H_6O_4$ , did not crystallise; its *semicarbazone*,  $C_5H_9O_4N_3$ , forms prisms, m. p. 211°: the *p-nitrophenylosazone*,  $C_{16}H_{14}O_6N_6$ ,

m. p. 297—299° (corr.). This compound was identical with the *p*-nitrophenylosazone prepared from the aldehyde produced on the oxidation of the natural hydroxyglutamic acid.  $\beta$ -Hydroxy- $\gamma$ -diethoxybutyric acid,  $C_8H_{12}O_5$ , clear oil, b. p. 120°/5 mm., possesses a sour odour. The *nitrophenylosazone* of the related tartronic semialdehyde,  $C_{15}H_{12}O_6N_6$ , m. p. 310° (corr.), forms rosettes of fine needles.

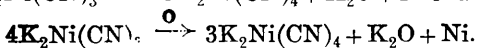
$\beta$ -Hydroxyglutamic acid in 4% solution in water has  $[\alpha]_D^{20}$  about +0.8°, but a 2% solution in hydrochloric acid has  $[\alpha]_D^{20}$  +16.3°. The rotation of the potassium salt is practically undetectable, but the addition of uranium nitrate renders it strongly levorotatory. *Strychnine d- $\beta$ -hydroxyglutamate*, prismatic needles, m. p. 245°,  $[\alpha]_D^{20}$  -26.3°. *Brucine d- $\beta$ -hydroxyglutamate*,  $C_{28}H_{35}O_9N_3$ , needles, decomp. about 200°,  $[\alpha]_D^{20}$  -25.0°. *Strychnine d-glutamate*,  $C_{26}H_{31}O_6N_3$ , glistening prisms, m. p. 225—230°, decomp. above 200°,  $[\alpha]_D^{20}$  -25.5°. *Brucine d-glutamate*,  $C_{28}H_{35}O_6N_3 \cdot 5H_2O$ , m. p. 101°, anhydrous salt, m. p. 240°, stout, prismatic needles with satin lustre,  $[\alpha]_D^{20}$  -23°. *Strychnine l-aspartate*,  $C_{25}H_{29}O_6N_3$ ,

fine needles, m. p. 252—255°,  $[\alpha]_D^{20} - 28.3^\circ$ . *Brucine 1-aspartate*,  $C_{27}H_{33}O_8N_3 \cdot 5H_2O$ , fine needles, m. p. 100°; anhydrous salt, m. p. 200°,  $[\alpha]_D^{20} - 28.4^\circ$ . *Strychnine 1- $\alpha$ -pyrrolidonecarboxylate*, fan-shaped masses of fine needles, m. p. 245°,  $[\alpha]_D^{20} - 26.7^\circ$ . *Brucine 1- $\alpha$ -pyrrolidonecarboxylate*, well-formed prisms, m. p. 180—185°, decomp. above 140°,  $[\alpha]_D^{20} - 31.5^\circ$ .

$\beta$ -Hydroxyglutamic acid was isolated to the extent of 2.4% from gliadin and 1.8% from glutelin. When administered to the phloridzinised dog,  $\beta$ -hydroxyglutamic acid yields 55—60% of its weight as dextrose, apparently three of its five carbon atoms being concerned in sugar formation. J. C. D.

**Preparation of Derivatives of Bromoacylised Carbamide Compounds.** FARBENFABRIKEN VORM. F. BAYER & Co. (Brit. Pat. 132795).—On treating bromoacylised carbamide compounds with acylising agents in presence of condensing agents, such as zinc chloride or sulphuric acid, acyl compounds are obtained which have a rapid but lasting sedative and soporific action. Examples are given of the preparation of *acetulbromo- $\alpha$ -ethylbutyrylcarbamide*, m. p. 108—109°, from bromo- $\alpha$ -ethylbutyrylcarbamide (474 parts), acetic anhydride (1000 parts), and zinc chloride (75 parts), the mixture being heated for one hour at 60° and then poured into iced water (3000 parts); of *acetulbromo- $\alpha$ -ethylbutyrylcarbamide*, m. p. 108—109°, from bromo- $\alpha$ -ethylbutyrylcarbamide and acetic anhydride; of *propionylbromo- $\alpha$ -ethylbutyrylcarbamide*, m. p. 103°; and of *benzoylbromo- $\alpha$ -ethylbutyrylcarbamide*, m. p. 139—140°, sulphuric acid being employed as condensing agent in each of the last three examples. G. F. M.

**Compounds of Univalent Nickel. III.** I. BELLUCCI (*Gazzetta*, 1919, 49, ii. 285—293).—Repetition of the work of Moore (compare A., 1894, i. 102; 1895, ii. 168) yields the following results. When treated in the hot with ammonium chloride solution, ordinary potassium nickelocyanide reacts only in virtue of the potassium cyanide it contains, the nickelous cyanide remaining unchanged:  $K_2Ni(CN)_4 + 2NH_4Cl = Ni(CN)_6 + 2KCl + 2NH_4CN$ . With the red nickelocyanide (compare A., 1919, i. 526), under similar conditions, two distinct reactions take place: (1) An oxidation, which depends on the marked tendency of the red salt to undergo conversion into the ordinary yellow nickelocyanide, and may follow one of the two schemes,  $4K_2Ni(CN)_3 \xrightarrow{2O} 3K_2Ni(CN)_4 + K_2O + NiO$  and

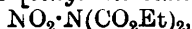


If the reaction is carried out in an inert medium or with the intervention solely of the combined oxygen of the water, as in Moore's experiments, the process of oxidation should proceed mainly according to the second of these two schemes. (2) Precipitation of nickelous cyanide as a result of the action of the ammonium chloride on the yellow potassium nickelocyanide formed in reaction (1). The oxidation (1) proceeds very rapidly, since the

ammonium chloride undergoes gradual hydrolysis and loss of ammonia, the hydrochloric acid thus liberated in the solution uniting with the potassium oxide formed during the oxidation. These conclusions are completely verified by the experimental results.

Moore's supposed suboxide,  $\text{Ni}_3\text{O}\cdot 2\text{H}_2\text{O}$ , consists of a mixture of pulverulent metallic nickel with hydrated nickelous oxide,  $\text{NiO}\cdot \text{Aq}$ .  
T. H. P.

**Preparation of the Tri- and Tetra-carboxylic Esters of Hydrazine and of Ethyl *as*-hydrazinedicarboxylate.** OTTO DIELS and ERICH BORGWARDT (*Ber.*, 1920, 53, [B], 150—158).—Dicarboxyethylnitroamide [ethyl nitroiminodicarboxylate],



b. p. 115—117°/14 mm., was prepared by the action of ethyl chloroformate on the potassium salt of nitrourethane in boiling toluene solution; attempts to reduce it to ethyl *as*-hydrazinedicarboxylate were unsuccessful, since ethyl iminodicarboxylate was formed with zinc dust in alcoholic solution or with sodium amalgam in moist ether, whilst the action of stannous chloride in ethereal solution in the presence of hydrogen chloride yielded the iminodicarboxylic ester and hydroxylamine hydrochloride. Better results were obtained by acting on the potassium derivative of ethyl benzylidenehydrazinecarboxylate with ethyl chloroformate, whereby ethyl benzylidenehydrazinedicarboxylate,  $\text{CHPh}\cdot\text{N}\cdot\text{N}(\text{CO}_2\text{Et})_2$ , prisms, m. p. 38—39° after softening at 37°, was obtained, which, when treated with phenylhydrazine in boiling aqueous-alcoholic solution, gave benzaldehydephenylhydrazone and ethyl *as*-hydrazinedicarboxylate, silvery prisms, m. p. 29—30°, b. p. 138—139°/12 mm. (the hydrochloride, m. p. 83·5° [? aq.], m. p. 107—108° [after desiccation over phosphoric oxide at 35°], was analysed). The ester was decomposed by distillation under ordinary pressure, yielding ethyl *s*-hydrazinedicarboxylate and a reddish-brown resin; it was converted by *o*-nitrobenzaldehyde into ethyl *o*-nitrobenzylidenehydrazinedicarboxylate, pale yellow crystals, m. p. 26—27°.

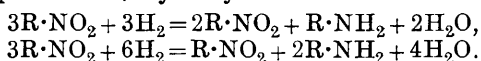
Ethyl *as*-hydrazinedicarboxylate was treated with ethyl chloroformate in dry ethereal solution, whereby a mixture of ethyl *as*-hydrazinedicarboxylate and ethyl hydrazinetricarboxylate was formed; the latter was transformed by the successive action of potassium and ethyl chloroformate in toluene solution into ethyl hydrazinetetracarboxylate, colourless, highly refractive, viscous oil, b. p. 145—146°/0·65 mm.

The preparation of ethyl hydrazinetricarboxylate, colourless, highly refractive oil, b. p. 184—186°/9 mm. (slight decomp.), was effected by the successive action of sodium and ethyl chloroformate on an ethereal solution of ethyl hydrazinecarboxylate (ethyl *s*-hydrazinedicarboxylate, long needles, m. p. 131°, was simultaneously formed), or by the interaction of ethyl chloroformate and ethyl *as*-hydrazinedicarboxylate. Investigation of the ester is not yet completed, but it has been shown that one ester group is readily

eliminated; thus, aqueous potassium hydroxide solution was found to convert it into ethyl *s*-hydrazinedicarboxylate and potassium carbonate,

$\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{N}(\text{CO}_2\text{Et})_2 + \text{H}_2\text{O} = \text{CO}_2 + \text{EtOH} + (\text{NH}\cdot\text{CO}_2\text{Et})_2$ ,  
whilst propylamine transformed it into a mixture of ethyl *s*-hydrazinedicarboxylate and *dipropylurethane*, colourless, pleasant-smelling liquid, b. p.  $83^\circ/10$  mm. H. W.

**Reduction of Aromatic Nitro-compounds by means of Platinum and Hydrogen.** G. CUSMANO (*Annali Chim. Appl.*, 1919, **12**, 123—130).—Aromatic nitro-compounds in ethereal solution are rapidly reduced to amines when shaken with platinum-black in an atmosphere of hydrogen. A gradual reduction through nitroso-compounds and hydroxylamines is thus effected in the case of nitroterpenes, whereas in the case of aromatic compounds only a mixture of amines and unaltered nitro-compounds is obtained. The reduction has been found to proceed as shown in the following equations in the case of *p*-nitrophenol, *p*-nitroanisole, *p*-nitrotoluene, *o*-nitrotoluene, and *m*-nitroaniline, although sufficient hydrogen was supplied for the formation of the intermediate nitroso-compounds or  $\beta$ -hydroxylamines:



The reduction of certain nitroso-compounds into hydroxylamines follows a similar course. The above-mentioned reactions do not agree with those obtained by reduction with ordinary chemical or electrochemical reagents, which proceed as follows:  $\text{R}\cdot\text{NO}_2 \rightarrow \text{R}\cdot\text{NO} \rightarrow \text{R}\cdot\text{NH}_2\text{O} \rightarrow \text{R}\cdot\text{NH}_2$ . The nitroso-compounds are always produced in small quantity, but under favourable conditions good yields of the  $\beta$ -hydroxylamines are obtained.  $\beta$ -Hydroxylamines offer more resistance than nitro-compounds to the action of ordinary reducing agents, but are reduced more readily than nitro-compounds by hydrogen and platinum-black. The velocity of the reduction of a  $\beta$ -hydroxylamine depends also on that of its transformation into the tautomeric form containing nitric nitrogen,  $\text{R}\cdot\text{NH}\cdot\text{OH} \rightleftharpoons \text{O}\cdot\text{NH}_2\text{R}$ . This transformation may become very rapid when the radicles in the hydroxylamine have no influence on either form, but in acid media, or in the presence of negative radicles tending to stabilise the first (aminic) form, there may be retardation of the reduction, so that the velocity of reduction, from being equal or superior to that of a nitro-compound, may become less than that of the latter. Preliminary experiments have shown that in the case of a mixture of *p*-nitrotoluene and azoxybenzene, the former is preferentially reduced. C. A. M.

**Remarkable Instance of Isomerism in the Naphthalene Series.** HARTWIG FRANZEN and FRITZ HELWERT (*Ber.*, 1920, **53**, [B], 319—322).—For investigation of the replaceability of the chlorine atoms in chloronitronaphthalenes, the authors have required 1-chloro-4-nitronaphthalene, pale yellow crystals, m. p.

85°, which they have prepared with difficulty in accordance with Atterberg's directions, and have confirmed his results. As, however, the yields are bad, they have also prepared it from 4-nitro- $\alpha$ -naphthamine by Sandmeyer's reaction as modified by Ullmann; in general, the product obtained in this manner was identical with that prepared by nitration of  $\alpha$ -chloronaphthalene, but on one occasion, without apparent variation in conditions, the substance which was isolated formed yellowish-green crystals, m. p. 60—61°, and gave analytical results agreeing with those required for 1-chloro-4-nitronaphthalene. This is not a case of physical isomerism, since it is not possible to convert the more fusible into the less fusible substance, and since also the two substances yield different *piperidino*-derivatives, yellowish-brown needles, m. p. 70—71°, and yellowish-brown needles, m. p. 63—64°, respectively, whilst also the rates of reaction with piperidine are very different in the two cases. As there appears to be no possible doubt as to the purity and uniformity of the starting materials, an instance of isomerism which is inexplicable by the aid of the generally accepted formula of naphthalene seems to be presented. Unfortunately, it has not been found possible up to the present to repeat the preparation of the isomeride, m. p. 60—61°. H. W.

**Synthesis of 3:10-Dichlorophenanthrene.** PAUL NYLÉN (*Ber.*, 1920, **53**, [B], 158—167).—The experiments were undertaken with the object of elucidating the constitution of some of the dichlorophenanthrenes obtained by Sandqvist and Hagelin (*A.*, 1919, i, 11); the substance described by these authors as II-10:3(6)-dichlorophenanthrene is found to be identical with 3:10-dichlorophenanthrene.

$\alpha$ -*p*-Chlorophenyl-*o*-nitrocinnamic acid, 
$$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \overset{\text{H}}{\underset{\text{H}}{\text{C}}} \cdot \text{CO}_2\text{H}$$
 is best obtained by heating potassium *p*-chlorophenylacetate with *o*-nitrobenzaldehyde and acetic anhydride, filtration from acid potassium acetate, and dilution of the filtrate with a regulated amount of water, whereby the acid is precipitated as pale yellow cubes, m. p. 190.2—190.7° (corr.). (The ammonium salt, yellow, lustrous needles, barium salt, yellow cubes, and calcium salt, prisms, are described.) Further dilution of the filtrates mentioned above yields a further precipitate, from which *allo*- $\alpha$ -*p*-chlorophenyl-*o*-nitrocinnamic acid, 
$$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \overset{\text{H}}{\underset{\text{H}}{\text{C}}} \cdot \text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4\text{Cl}$$
 m. p. 148.5—150° (corr.),

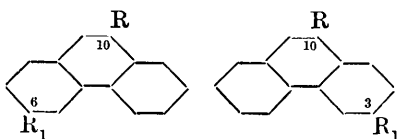
is isolated. The substance is characterised as the *allo*-acid by its lower melting point, the greater solubility of its salts (the ammonium salt is described), its non-isomerisation by iodine, its sensibility to the action of light, and the formation of a compound with aniline, yellow needles, m. p. 124°.

$\alpha$ -*p*-Chlorophenyl-*o*-aminocinnamic acid is formed in a yellow and a colourless modification, both of which have m. p. 224°, by the reduction of the nitro-acid with ferrous sulphate and ammonia (the hydrochloride, sulphate, and ammonium, calcium, and barium salts are described), and is transformed by acetic anhydride in the

presence of concentrated sulphuric acid into  $\beta$ -p-chlorophenyl-carbostyryl, long, colourless needles, m. p.  $258.5-259.5^\circ$  (corr.). Diazotisation converts the amino-acid into  $\alpha$ -p-chlorophenyl-o-diazocinnamic acid, yellow flocks, which are stable at the ordinary temperature but explode at  $101^\circ$ , from which 3-chlorophenanthrene-10-carboxylic acid, colourless needles, m. p.  $301.5-302.5^\circ$ , is best obtained by the use of copper powder (the calcium, barium, copper, iron, and silver salts are described). Distillation under diminished pressure effects the partial conversion of the acid into 3-chlorophenanthrene, m. p.  $80-81^\circ$ , whilst oxidation with chromic acid converts it into 3-chlorophenanthraquinone, yellow needles, m. p.  $264.5-265^\circ$  (corr.) (compare Sandqvist and Hagelin, *loc. cit.*). Ethyl 3-chlorophenanthrene-10-carboxylate crystallises in long, colourless, shining needles, m. p.  $94.5-95^\circ$ , and is converted by hydrazine hydrate into the corresponding hydrazide, m. p. about  $270^\circ$ , which, with benzaldehyde and acetone, respectively, yields the corresponding benzylidene derivative, colourless, prismatic needles, m. p.  $248-249^\circ$  (corr.), and isopropylidene derivative, long, colourless needles, m. p.  $243-245^\circ$  (corr.). Diazotisation of the hydrazide is best effected by nitrous fumes, and yields the corresponding azide, m. p. about  $96^\circ$  (decomp.). The latter is converted by boiling absolute alcohol into 3-chloro-10-phenanthryl-urethane,  $C_{14}H_8Cl \cdot NH \cdot CO_2Et$ , colourless, slender needles, m. p.  $197.5^\circ$  (corr.) after previous softening, which, on treatment with boiling concentrated hydrochloric acid, yields 3-chloro-10-amino-phenanthrene, pale yellow prisms and needles, m. p.  $141.2-142.2^\circ$  (corr.). [The hydrochloride, m. p. about  $230^\circ$ , and the mono-benzoyl derivative, colourless, silky needles, m. p.  $257.5^\circ$  (corr.), are described.] Diazotisation of the amine and treatment of the yellow diazonium compound with cuprous chloride leads to the formation of 3:10-dichlorophenanthrene, colourless, slender needles, m. p.  $117-117.5^\circ$  (corr.), in rather poor yield. H. W.

### Constitution of Two Series of Doubly Substituted Phenanthrene Derivatives. 3:9-Dibromophenanthrene.

HÅKAN SANDQVIST (*Ber.*, 1920, 53, [B], 168-171).—In previous communications, several disubstituted phenanthrenes have been described in which one substituent is present in the bridge (say in position 10), the other in position 3 or 6; two genetic series have thus been prepared, which have been provisionally designated I and II. The allocation of the annexed formulæ to the members



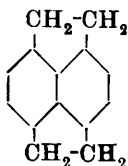
of the two series is rendered difficult, since the atom in the bridge is affected by oxidation, and the frequently assumed aliphatic character of the linking in the bridge is not

such as to allow the ready replacement of the substituting atom by other groups. The synthesis of 3:10-dichlorophenanthrene by Nylen (preceding

abstract) has, however, shown that this substance is identical with II-10 : 3(6)-dichlorophenanthrene obtained by Sandqvist and Hagelin (A., 1919, i, 11), so that all derivatives belonging to the I series are 10:6(=9:3)-compounds, whilst those belonging to the II series are 10:3(=9:6)-substances.

Potassium 10-bromophenanthrene-6-sulphonate is converted by phosphorus pentabromide into 10-bromophenanthrene-6-sulphonyl bromide, yellow prisms, m. p. 202—203° (slight decomp.), which is converted by further action of the same reagent into 3:9-di-bromophenanthrene, pale yellow needles and prisms, m. p. 143—143·5°. Chromic acid converts the latter into 3-bromophenanthraquinone.  
H. W.

**The Acenaphthene Series. I.** FRITZ MAYER and WALDEMAR KAUFMANN (*Ber.*, 1920, **53**, [B], 289—298).—The experiments were undertaken with the twofold object of preparing technically valuable derivatives of acenaphthene and of synthesising *aceacenaphthene* (annexed formula); the latter purpose has not been effected up to the present.

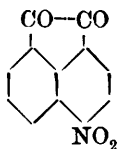


Dibromoacenaphthene tetrabromide, colourless crystals, m. p. 179—180°, is prepared by the addition of a solution of bromine in chloroform to a boiling solution of acenaphthene in the same solvent; it is converted by boiling concentrated alcoholic potassium hydroxide solution into *tetrabromoacenaphthene*,

orange crystals, m. p. 180—181°.

5-Ethylacenaphthene is obtained as an oil, b. p. ca. 166°/20 mm., 310°/atmos. pressure, by the action of ethyl bromide on acenaphthene in the presence of aluminium chloride. The corresponding *picrate* forms red crystals, m. p. 95—96°. The constitution of the hydrocarbon is deduced from its oxidation through 4-ethylnaphthalene-1:8-dicarboxylic anhydride, m. p. 180°, to the previously described anhydride of naphthalene-1:4:8-tricarboxylic acid, m. p. 248°. Bromination of 5-ethylacenaphthene gives a yellow oil, b. p. above 170°/vac., which remains unchanged when boiled with an excess of alcoholic potassium hydroxide solution. Distillation of 5-ethylacenaphthene with zinc dust yields acenaphthylene.

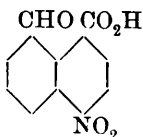
5-Chloroacetylacenaphthene, m. p. 104°, is prepared by the action of chloroacetyl chloride on the hydrocarbon in the presence of aluminium chloride. Nitration of 5-acetylacenaphthene by nitric acid (D 1·39) in the presence of glacial acetic acid gives 1-nitro-5-acetylacenaphthene, m. p. 204°. Pyridino-4:5-acenaphthene has m. p. 60—61°, whereas Zinke and Raith (this vol., i, 89) give 67°.



5-Nitroacenaphthene-1:2-quinone (annexed formula), slender, yellow needles, m. p. 199°, is prepared by the nitration of acenaphthenequinone by concentrated sulphuric acid and nitric acid (D 1·51). (The *mono* and *di-phenylhydrazones* form dark reddish-brown needles, m. p.



186°, and darker crystals, m. p. 148°, respectively.) The quinone is oxidised by sodium dichromate in the presence of glacial acetic acid to 4-nitronaphthalene-1:8-dicarboxylic acid, the anhydride of which has m. p. 220°. Concentrated potassium hydroxide solution converts the nitroquinone into 4(?)5-nitronaphthalaldehydic acid (annexed formula), m. p. 245—247°.



5:6-Dinitroacenaphthene-1:2-quinone, m. p. above 300° (slow decomp.), is prepared by the more energetic nitration of acenaphthenequinone, and is oxidised by sodium dichromate in boiling glacial acetic acid solution to the anhydride of 4:5-dinitronaphthalene-1:8-dicarboxylic acid, m. p. above 300°; the latter substance (m. p. 310°) appears also to be formed by the oxidation of 5:6-dinitroacenaphthene.

H. W.

**Preparation of Aromatic Nitro-compounds of Retene and its Homologues.** ROBERT ARNOT (D.R.-P. 315623; from *Chem. Zentr.*, 1920, ii, 188—189).—Retene or retenequinone, or a resin oil of high boiling point, particularly tar tallow, is treated with nitric acid (D greater than 1.43) in the presence or absence of fuming sulphuric acid. *Dinitroretene*, from retene or tar tallow and red, fuming nitric acid or concentrated nitric acid (D 1.48—1.52) at 15°, forms a lemon-yellow, flocculent precipitate; the diazonium compound derived from the corresponding amine yields azo-dyes with suitable components. *Dinitroretenequinone*, from the quinone, gives an olive-green solution in alcoholic alkali, which becomes red when warmed and green again when cooled; the hot alcoholic solution of dinitroretenequinone becomes red on addition of alkali. *Nitroretenesulphonic acid*, from retene, 20% oleum, and nitric acid, forms a yellowish-brown precipitate.

H. W.

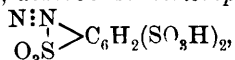
**Fluidities and Volumes of some Nitrogenous Organic Compounds.** EUGENE C. BINGHAM, HENRY S. VAN KLOOSTER, and WALTER G. KLEINSPEHN (*J. Physical Chem.*, 1920, **24**, 1—20. Compare A., 1910, ii, 395).—The liquids examined were very carefully purified, and their corrected boiling points are recorded, as follows: benzonitrile 190.7°, *o*-toluidine 198.2°, aniline 182.7°, diethylaniline 212°, dimethylaniline 192.37° (m. p. 2.1°), ethylaniline 203.6°, methylaniline 194.7°, and nitrobenzene 209.3°; these differ in many cases from the generally accepted values. The density and viscosity have been determined at intervals of 10° over the temperature range 0—100°. The experimental results show that aniline is considerably associated: substitution of groups in the benzene nucleus has but little effect on the association, whilst successive substitution in the amino-group reduces the association progressively. The atomic constant for nitrogen in aniline at a fluidity of 200 is 3.4, but it remains an open question whether it has the same value in nitriles and nitro-compounds. Mixtures of aniline and dimethylaniline follow the additive fluidity rule fairly closely.

J. F. S.

**Trisulphanilic [Aniline-2 : 4 : 6-trisulphonic] Acid.** S. C. J. OLIVIER (*Rec. trav. chim.*, 1920, **39**, 194—199).—When aniline-*p*-sulphonic acid (100 grams) is heated with 600 c.c. of a mixture of one part of phosphoric oxide and three parts of sulphuric acid at 180° for eight hours, *aniline-2 : 4 : 6-trisulphonic acid* is obtained and isolated as its *barium salt*,  $[\text{C}_6\text{H}_2(\text{NH}_2)(\text{SO}_3)_3]_2\text{Ba}_3 + 10\text{H}_2\text{O}$ . The free *acid* crystallises with  $4\text{H}_2\text{O}$ , is very hygroscopic, and gives a *sodium salt*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_2(\text{SO}_3\text{Na})_3 \cdot 2\text{H}_2\text{O}$ ; a *potassium salt*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_2(\text{SO}_3\text{K})_3 \cdot \text{H}_2\text{O}$ , and a *potassium hydrogen salt*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_2(\text{SO}_3\text{K})_2 \cdot \text{SO}_3\text{H}$ .

When the acid is diazotised in acid solution with potassium nitrite, or when its potassium salt is diazotised by a current of nitrogen trioxide, it gives a stable diazo-salt, *potassium diazobenzenetrisulphonate*,  $(\text{SO}_3\text{K})_2\text{C}_6\text{H}_2\text{N} \begin{smallmatrix} \text{N} \\ \text{SO}_3 \end{smallmatrix}$ , which is only slowly decomposed in Gattermann's reaction, giving 1-chlorobenzene-2 : 4 : 6-trisulphonic acid, yielding an *acid chloride*,  $\text{C}_6\text{H}_2\text{Cl}(\text{SO}_2\text{Cl})_3$ , m. p. 171—171·5°, which, when heated in a sealed tube with phosphorus pentachloride at 200—210° for three hours, yields 1 : 2 : 4 : 6-tetrachlorobenzene.

If anilinetrisulphonic acid itself is diazotised in alcoholic solution with nitrogen trioxide, it yields, after distilling off the alcohol under reduced pressure, *diazobenzenetrisulphonic acid*,



which, when boiled with alcohol, gives benzene-1 : 3 : 5-trisulphonic acid.

W. G.

**Preparation of Condensation Products from Formaldehyde and Primary Aromatic Amines.** ALEXANDER M. NASTUKOV and PETER M. CRONEBERG (D.R.-P. 308839; from *Chem. Zentr.*, 1918, ii, 999—1000).—Primary aromatic amines are treated with formaldehyde, preferably in slight excess, in the presence of boiling dilute mineral acids, such as hydrochloric or sulphuric acid; the theoretical yields of amino-bases, free from oxygen and resin and of constant m. p., are thus obtained, which develop on the fibre azo-dyes of red, Bordeaux-red, khaki-brown, or yellow shades. The colours obtained are fast to alkalis, acids, and washing. The *amino-base* from *o*-toluidine, formaldehyde, and sulphuric acid is an amorphous, pale yellow precipitate, m. p. 110—111°. Formaldehyde yields with aniline an amorphous, brownish-yellow *base*, m. p. 114—115°, with technical xyldine a *base*, m. p. 58·5—59·5°. with *o*-anisidine an amorphous, pale yellow *compound*, m. p. 133—134°, and with *m*-toluidine a *base*, m. p. 169—170°.

H. W.

**Molecular Organic Compounds. III.** M. GIUA and F. CHERCHI (*Gazzetta*, 1919, **49**, ii, 264—285. Compare A., 1917, i, 386).—Investigations have been made on the binary systems formed by diphenylamine with *o*-nitrophenol, *s*-trinitrophenol, azo-

benzene, *n*-cetyl alcohol, 2:4-dichloroaniline, *s*-trichlorophenol, and benzophenone.

The system diphenylamine-*o*-nitrophenol exhibits a single eutectic point at the concentration 51% of the nitrophenol and the m. p. 21·6°. The fused mixtures of the two components show clearly the general phenomenon observed with mixtures of diphenylamine and aliphatic or aromatic nitro-compounds (compare Ciusa and Vecchiotti, A., 1912, i, 755; Pushin and Grebenschtschikov, A., 1913, ii, 105; Tinkler, T., 1913, **103**, 2171; Giua, A., 1915, i, 659; 1916, i, 205; Gomborg and Schoepfle, A., 1917, i, 551), the addition of a small proportion of *o*-nitrophenol sufficing to impart an intense red coloration to diphenylamine.

The results obtained with the system diphenylamine-*s*-trinitrophenol indicate the formation of a compound which contains the components in the molecular ratio 1:1, and dissociates on melting. The intense red coloration persists even after solidification of the mixtures, but gradually changes to a greenish-yellow, which is still evident after the solid mass has remained for some days at about 25° (compare Walker, T., 1896, **69**, 1341).

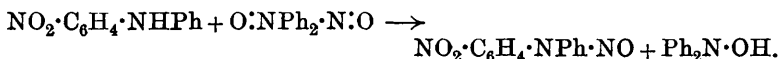
The system diphenylamine-azobenzene exhibits only one eutectic point. The addition of azobenzene in small proportion to diphenylamine results in an intense dark red coloration, but the formation of an additive compound is excluded. The auxochrome group, ·N:N·, of the azobenzene functions, as regards colour, quite similarly to the nitro-group.

Cetyl alcohol, 2:4-dichloroaniline, and *s*-trichlorophenol show no peculiarities in their behaviour towards diphenylamine, the solidification curves possessing one eutectic point in each case. In the cetyl alcohol system, the solidifying point of diphenylamine is lowered from 53·1° to about 38° by addition of 68·99% of the alcohol; mixtures of the two compounds in the hot form pale yellow solutions. For the system diphenylamine-2:4-dichloroaniline, the eutectic corresponds with the concentration 44% of the aniline, and melts at about 44°; fused mixtures of the two components are colourless.

Benzophenone and diphenylamine combine in the molecular proportions 1:1 to form a pale yellow additive compound, m. p. 30·85°, which must be classed with the molecular compounds containing auxochromes (compare Kauffmann, "Die Valenzlehre." Stuttgart, 1911, 509). The eutectic between the additive compound and diphenylamine has m. p. about 28·7°, and that between the compound and benzophenone m. p. about 24°. T. H. P.

**Derivatives of Quadrivalent Nitrogen.** HEINRICH WIELAND and KARL ROTH (*Ber.*, 1920, **53**, [B], 210—230).—The behaviour of diphenylnitric oxide (Wieland and Offenbächer, A., 1914, i, 955) towards other radicles, such as nitric oxide, nitrogen peroxide, triphenylmethyl, and a derivative of diphenylnitrogen, has been investigated, and the unstable di-*p*-tolylnitric oxide has been prepared and examined in a similar direction.

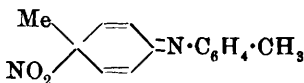
Diphenylhydroxylamine is prepared by a slight modification of the method of Wieland and Roseeu (A., 1912, i, 253), and is transformed into diphenylnitric oxide, m. p.  $64^{\circ}$  (compare Wieland and Offenbächer, *loc. cit.*), which, when quite pure, can be preserved in ethereal solution during twenty-four hours without undergoing alteration. When its ethereal solution is treated with nitric oxide at  $0^{\circ}$ , a mixture of *p*-nitrodiphenylnitrosoamine and diphenylnitrosoamine is formed. Apparently the first stage of the reaction consists in the addition of nitric oxide to yield the compound  $\text{O:NPh}_2\cdot\text{N':O}$  (which is analogous to  $\text{N}_2\text{O}_3$ ); this probably is converted successively into the isomeric diphenylnitroamine and *p*-nitrodiphenylamine,  $\text{Ph}_2\text{N}\cdot\text{NO}_2 \rightarrow \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHPh}$ ; the secondary amine is then converted into its nitroso-derivative according to the scheme:



The diphenylamine, which is isolated as its nitroso-derivative, is formed by the auto-decomposition of diphenylhydroxylamine. That a compound analogous in its action to nitrogen trioxide is actually formed is shown by the fact that if the experiment is repeated in the presence of diphenylamine or di-*p*-tolylamine, the nitroso-derivatives of these substances are formed in large quantity.

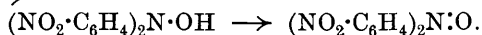
Diphenylnitric oxide reacts with triphenylmethyl to yield the compound,  $\text{Ph}_2\text{N}\cdot\text{O}\cdot\text{CPh}_2\langle\bigcirc\rangle\text{CPh}_3$ , m. p.  $160^{\circ}$ , the constitution of which is deduced from its catalytic hydrogenation to diphenylamine and the carbinol of Ullmann and Borsum's "hexaphenylethane," which Tschitschibabin (A., 1905, i, 125) has shown to be *p*-benzhydryltetraphenylmethane. The course of the reaction is remarkable, since the simple additive product first formed appears to be so strongly unsaturated that it combines with a second molecule of triphenylmethyl; the hydrogen which is thus liberated reacts with a second molecule of diphenylnitric oxide, so that the molecular ratio 1:1 is preserved, as is experimentally demonstrated to be the case.

*Di-p-tolylnitric oxide*, red needles, m. p.  $59-60^{\circ}$ , is prepared by oxidising di-*p*-tolylhydroxylamine (Wieland and Roseeu, A., 1915, i, 797) with dry silver oxide; even when placed in a vacuum and removed from light, the substance cannot be preserved for more than three hours; after a few hours it yields a dark, semi-crystalline mass, from which di-*p*-tolylamine can be extracted. With nitric oxide it yields a pale yellow, crystalline, somewhat unstable compound,  $\text{C}_{14}\text{H}_{14}\text{O}_2\text{N}_3$ , m. p.  $93^{\circ}$ , which is not identical with *o*-nitroditolylamine; the substance could not be reduced to ditolylhydrazine or ditolylamine and ammonia, so that it is not ditolyl-nitroamine. It is provisionally assumed to have the annexed formula.



Di-*p*-tolylhydrazine is converted by nitrogen peroxide into 2:2'-dinitrodi-*p*-tolylamine, cinnabar-red needles, m. p. 192—193° (decomp.).

Di-*p*-nitrophenylnitric oxide,  $(\text{NO}_2 \cdot \text{C}_6\text{H}_4)_2\text{N} \cdot \text{O}$ , dark red crystals, is prepared by the action of nitrogen peroxide on diphenylnitric oxide, or, more conveniently, on diphenylhydroxylamine. It has m. p. 109° (decomp.) and is remarkably stable, since it can be preserved without change during three months. Its formation probably occurs according to the scheme:  $\text{Ph}_2\text{N} \cdot \text{O} + \text{NO}_2 \rightarrow \text{O} \cdot \text{NPh}_2 \cdot \text{NO}_2 \rightarrow \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NPh} \cdot \text{OH} \rightarrow \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NPh} \cdot \text{O} \rightarrow (\text{NO}_2 \cdot \text{C}_6\text{H}_4)_2\text{NPhO} \cdot \text{NO}_2 \rightarrow$



It is reduced by stannous chloride and hydrochloric acid to 4:4'-diaminodiphenylamine, and by phenylhydrazine to di-*p*-nitrophenylhydroxylamine, orange-yellow needles, m. p. 90° (decomp.); the latter is markedly acidic in character and yields two series of salts, giving, for example, with an ethereal solution of phenylhydrazine a pale orange compound, m. p. 126° (decomp.), and with aqueous ammonia or with alkalis intensely deep blue solutions. The use of phenylhydrazine as a reducing agent in this connexion is of particular interest, since other agents transform the oxide directly into the secondary amine. Di-*p*-nitrophenylnitric oxide reacts with nitric oxide to yield a substance which has all the properties expected of di-*p*-nitrophenylnitroamine; it is, however, decomposed by crystallisation from ethyl acetate, yielding 4:4'-dinitrodiphenylamine, m. p. 213—215°; it combines with triphenylmethyl to yield NN-di-*p*-nitrophenyl-O-triphenylmethylhydroxylamine,  $(\text{O}_2\text{N} \cdot \text{C}_6\text{H}_4)_2\text{N} \cdot \text{O} \cdot \text{CPh}_3$ , pale yellow, rhombic platelets, m. p. 180° (decomp.), which is reduced by hydrogen in the presence of palladium-black to 4:4'-diaminodiphenylamine and triphenylcarbinol.

Diphenylnitric oxide is remarkably stable towards water and alkalis, but is rapidly converted by 2*N*-hydrochloric acid into diphenylamine and quinoneanil oxide,  $\text{O}=\langle \text{C}_6\text{H}_4 \rangle=\text{NPh} \cdot \text{O}$ , shining prisms with a pale brown surface coloration, m. p. 142° (the latter is reduced by zinc dust in glacial acetic acid solution to *p*-hydroxydiphenylamine, which is converted by dry silver oxide into quinoneanil, m. p. 98°). For some unexplained reason, ethereal solutions of diphenylnitric oxide occasionally undergo the same change spontaneously.

The stability of the diarylnitric oxide diminishes from the dinitrophenyl through the phenyl to the di-*p*-tolyl derivative; the stability of the di-*p*-anisyl compound described by Meyer and Gottlieb-Billroth (this vol., i, 38) is therefore remarkable. H. W.

**The Transformation of Dinitrophenolsulphonic Acids into Picric Acid.** M. MARQUEYROL, P. CARRÉ, and P. LORLETTE (*Bull. Soc. chim.*, 1920, [iv], 27, 140—143).—The transformation of 2:6-dinitrophenol-*p*-sulphonic acid into picric acid is more rapid

than that of the 2:4-dinitrophenol-*o*-sulphonic acid. It is thus preferable, in the manufacture of picric acid, to use a sulphonated phenol mixture containing the maximum amount of phenol-2:4-disulphonic acid.

W. G.

**The Preparation of Picric Acid by the Process with Nitric Acid using Nitric Acids of Different Concentrations.** M. MARQUEYROL, P. CARRÉ, and P. LORIETTE (*Bull. Soc. chim.*, 1920, [iv], 27, 143—148).—By arranging completely to utilise the nitric acid used, it is possible to obtain good yields of picric acid by sulphonating 100 grams of phenol with 350 grams of 92.5% sulphuric acid, heating the mixture on a water-bath for three hours, and then nitrating the mixture with five molecular proportions of nitric acid (D 1.273). Under laboratory conditions, it does not seem possible to use less than these proportions of sulphuric and nitric acids.

W. G.

**Equilibrium Diagrams of Binary Mixtures of Picric Acid, Trinitrotoluene, Dinitrotoluene, and Mononitronaphthalene.**

A. WOGRINZ and P. VÁRI (*Z. ges. Schiess. u. Sprengstoffw.*, 1919, 14, 249—251, 267—270; from *Chem. Zentr.*, 1920, i, 115).—The cooling curves have been deduced from experiments performed in a special type of apparatus, which is fully described, and is designed to secure closely similar external conditions. The curves are given for the systems: picric acid-dinitrotoluene, tri- and dinitrotoluenes, trinitrotoluene-nitronaphthalene.

H. W.

**Modern Shattering Nitro-explosives.** C. F. VAN DUIN and B. C. ROETERS VAN LENNEP (*Rec. trav. chim.*, 1920, 39, 145—177).—The authors have examined nineteen nitro-compounds of different types, capable of being used as explosives, to determine their stability, temperature of explosion, and sensitiveness to mechanical shock, and thus to determine the influence of constitution on these properties.

For the stability test, the Dutch method has been used, which consists in heating 10 grams of the substance in a special flask at 95° first for three hours, and if no decomposition occurs, for eight hours per day up to a period of thirty days. Under these conditions, trinitrophenylmethylnitroamine, trinitroaminophenol, trinitroaminoanisole, trinitroaminophenetole, trinitro-*m*-phenylenediamine, trinitromethylnitroaminophenol, aminotritrophenylmethylnitroamine, hexanitrodiphenyl sulphide and sulphone, and dipicrylamine stood the test. Tetranitroaniline showed marked decomposition after twenty-six hours at 60°, whilst tetranitrophenylmethylnitroamine was even less stable, the substance containing the most active nitro-group being thus the least stable. Tetranitrophenol showed signs of decomposition after four hours at 70°. In general, the 2:3:4:6-tetranitro-derivatives decompose rapidly either at high temperatures or at the ordinary temperature, this being probably due to the splitting off of the nitro-group in

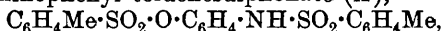
position 3. Stettbacher's view (compare *Z. ges. Schiess. u. Sprengstoffw.*, 1916, **11**, 114) that the nitrous acid evolved in the decomposition of tetranitroaniline comes from an action between the amino- and the *o*-nitro-groups is incorrect. The instability of substances with mobile nitro-groups is due to these mobile groups, and a methylnitroamino-group also exerts an unfavourable influence on the stability of a compound.

In determining the temperature of explosion, it is advisable to determine the figure by two methods, one in which the temperature is raised above 100° by 20° a minute, and the second in which it is only raised 5° a minute, in order to get a correct idea of the behaviour of the explosives. There is apparently no definite relationship between the explosion temperature and the stability of a compound. In the case of substances which decompose at their melting point, the decomposition and explosion temperatures are generally almost equal.

For testing such nitro-explosives for their sensitiveness to shock, the authors find Kast's method (compare *Z. ges. Schiess. u. Sprengstoffw.*, 1909, **4**, 263) quite satisfactory. The introduction of a methylnitroamino-group or of a fourth nitro-group notably increases the sensitiveness to shock, whilst an amino-group lowers it. The etherification of a phenol diminishes its sensitiveness. Apart from the nature of an entrant group, its mobility, in the case of highly nitrated substances, exerts a marked influence, mobility increasing sensitiveness. The replacement of a fixed nitro-group by a mobile group produces a remarkable influence on the sensitiveness, as is shown by a comparison of dipicrylamine with 2:4:6:2':3':4'-hexanitrodiphenylamine.

W. G.

**Esters of *N*-Arylsulphonyl-*N*-alkylaminoaryl Esters.** E. REBER and J. SIEGWART (U.S. Pat. 1316804).—*N*-Toluenesulphonyl-*p*-aminophenyl toluenesulphonate (*A*),



is dissolved in aqueous sodium hydroxide, and, on cooling the hot solution, the sodio-derivative crystallises. This is converted almost quantitatively into the *N*-methyl derivative of *A*, needles, m. p. 162°, by heating for several hours at 100–120° with methyl chloride and methyl alcohol. Other alkylating agents may be used, such as ethyl haloids (m. p. 117°), allyl bromide (m. p. 113°), ethylene dibromide, or benzyl bromide (m. p. 142°), with alcohol or water as diluent (the m. p. of the derivative of *A* produced is given in brackets). Corresponding derivatives of *o*- or *m*-aminophenol, or of the aminonaphthols and their substitution products, which are substituted in the amino-group by an arylsulphonyl radicle and in the hydroxyl group by an acyl radicle, can also be easily alkylated.

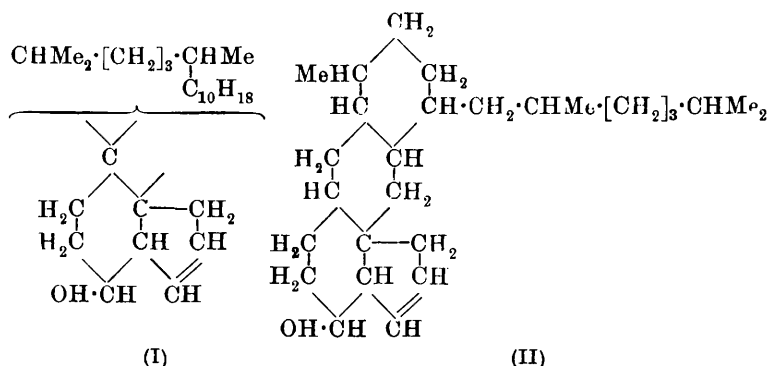
CHEMICAL ABSTRACTS.

**Catechol.** BENNO ELSNER (*Monatsh.*, 1919, **40**, 361–362).—At dilutions not greater than 1%, with excess of cold barium hydroxide solution, catechol gives a precipitate of a very sparingly

soluble *barium* salt,  $C_6H_4O_2Ba \cdot 3\frac{1}{2}H_2O$ , in the form of silver-grey leaflets with a pearly lustre. Since resorcinol and quinol do not give such a precipitate, the reaction is suggested as a means of separation, which is probably superior to that which depends on the use of benzene.

J. K.

**Constitution of Cholesterol.** A. WINDAUS (*Nachr. K. Ges. Wiss. Göttingen*, 1919, 237—254; from *Chem. Zentr.*, 1920, i, 82). —The author gives a general account of the investigations which have, in part, served to elucidate the constitution of cholesterol. In comparison with the formulæ of the original communications, the present formulæ are increased by the addition of two atoms of hydrogen, since this alteration has been shown to be necessary for the acid,  $C_{26}H_{44}O_3$ , obtained by the oxidation of cholestenone by potassium permanganate (compare A., 1917, i, 265). If the presence of an octyl radicle (Windaus and Resau, A., 1913, i, 615) be regarded as established, the constitution of cholesterol may be expressed by formula I:



Two saturated ring systems must be present in the residue which contains ten carbon atoms, and these probably have certain carbon atoms in common with the rings of formula I. Although complete evidence with regard to certain details is lacking, it is possible to put forward a constitutional formula which gives an approximately accurate picture of the arrangement of the carbon atoms. A possible constitution is shown by formula II.

H. W.

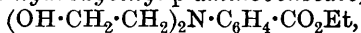
**Solubility of Microbic Acid [*p*-Chlorobenzoic Acid].** R. OTTO (*Konserven Zeit*, 1917, 18, No. 1; *Landw. Jahrb.*, 52; *Erg. Bd.* 1, 85—86; from *Chem. Zentr.*, 1919, iii, 1052—1053). —The solubility of *p*-chlorobenzoic acid is given by Seeger as 1:2500 and by Beilstein as 1:5288; the author finds the acid to be much more sparingly soluble than these figures would indicate, and that 25,000 parts of water do not completely dissolve 1 part of it. Failure to detect the presence of *p*-chlorobenzoic acid in alcohol-free fruit juices which have been treated with microbin is therefore readily explicable.

H. W.



**Catalytic Preparation of Amides.** A. MAILHE and (MME) BELLEGARDE (*Caoutchouc et Gutta-percha*, 1919, **16**, 9947—9948; from *Chem. Zentr.*, 1919, iii, 952).—Although aromatic amines react readily with aliphatic and aromatic acids to yield substituted amines, the esters, such as methyl benzoate, can be boiled with aniline for a protracted period without forming an appreciable amount of the amide. It is now shown that substituted amines may be readily produced when an equimolecular mixture of ester and amine is allowed to react in the presence of aluminium oxide or thorium oxide at 480—490°. Amides, but not nitriles, are obtained when a mixture of ammonia and the vapour of an acid anhydride is passed over the same catalysts at 450°, and a similar change is observed when an ester is used in place of the anhydride. At a higher temperature, larger amounts of nitriles are produced in certain circumstances. The following examples are cited. Benzanilide is prepared from aniline and methyl or ethyl benzoate, the yield being 40—50% of the quantity of ester used; the three isomeric benzotoluidides from benzoic ester and the requisite toluidine; *benzocyclohexylamide*,  $C_6H_{11}\cdot NH\cdot CPh$ , m. p. 153°, from methyl benzoate and *cyclohexylamine*; *phenylpropionanilide*; *cuminanilide*; *acetanilide* and its homologues from aniline and the corresponding aliphatic esters. The following compounds are obtained by the use of gaseous ammonia. Propionamide and *isovaleramide* from the corresponding anhydrides; *salicylamide* from methyl salicylate (in this instance the formation of nitrile is not observed if the catalyst is heated to 500°). H. W.

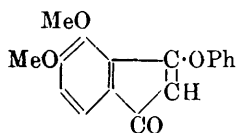
**Preparation of New Mono- and Di- $\beta$ -hydroxyethylamino-benzoic Esters.** SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat. 128552).—Mono- and di- $\beta$ -hydroxyethylaminobenzoic esters are obtained by heating to temperatures varying from 50° to 110° a mixture of ethylene oxide and an aminobenzoic ester in molecular proportion of one or two of ethylene oxide respectively to one of ester. The reaction can be accelerated by the addition of small quantities of water or ethyl alcohol. Thus *ethyl  $\beta$ -hydroxyethyl-p-aminobenzoate*,  $OH\cdot CH_2\cdot CH_2\cdot NH\cdot C_6H_4\cdot CO_2Et$ , a colourless, crystalline substance, melting at 63° and boiling at 213—214°/4 mm., is produced by heating for several hours in a closed vessel at 50° equimolecular proportions of ethylene oxide and ethyl *p*-aminobenzoate, whilst if under similar conditions 2 mols. of ethylene oxide are used, together with  $\frac{1}{2}$  mol. of water and 1 mol. of ethyl alcohol, *ethyl di- $\beta$ -hydroxyethyl-p-aminobenzoate*,



is obtained. After crystallisation from benzene it forms white lamellæ, m. p. 94° and b. p. 246°/4 mm. G. F. M.

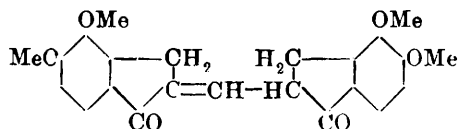
**2 : 3-Dimethoxyphenylpropionic Acid and 4 : 5-Dimethoxyhydrindone.** S. RUHEMANN (*Ber.*, 1920, **53**, [B], 274—284).—Ethyl 2 : 3-dimethoxycinnamate (compare Perkin and Robinson, T., 1914, **105**, 2387; Kranichfeldt, A., 1914, i, 190), colourless

prisms, m. p. 45—46°, b. p. 184—185°/15 mm., is prepared by the action of ethyl acetate and sodium on 2:3-dimethoxybenzaldehyde; it readily absorbs bromine to yield the corresponding dibromo-ester, but, at the same time, a certain amount of hydrogen bromide is invariably eliminated. The crude ester, which could not be purified, is converted by alcoholic potassium hydroxide solution into 2:3-dimethoxyphenylpropionic acid,  $C_8H_5(OMe)_2 \cdot C:C \cdot CO_2H$ , colourless prisms, m. p. 108—109°. In a similar manner to 4-methoxy-1-naphthylpropionic acid (this vol., i, 326), the latter is transformed by alcohol and hydrogen chloride into *ethyl*  $\beta$ -chloro-2:3-dimethoxycinnamate, colourless oil, b. p. 190—191°/12 mm., which, when treated with sodium phenoxide, gives *ethyl*  $\beta$ -phenoxy-2:3-dimethoxycinnamate, pale yellow, viscous oil, b. p. 242—244°/12 mm. Hydrolysis of the latter yields the two stereo-isomeric  $\beta$ -phenoxy-2:3-dimethoxycinnamic acids, coarse, colourless crystals, m. p. 192—193° (decomp.), and silky needles, m. p. 137—138°, respectively, which can be comparatively readily separated by fractional crystallisation from alcohol. Instead of the



expected flavone, either isomeride, when acted on by phosphorus pentachloride and aluminium chloride successively, yields 3-phenoxy-4:5-dimethoxyindone (annexed formula), colourless, shining leaflets, m. p. 199—200°, the constitution of which is deduced from its conversion by hydriodic acid into phenol and 4:5-dihydroxyindane-1:3-dione, colourless needles, m. p. 277—278° (decomp.), the white, unstable *silver* salt of which is also described.

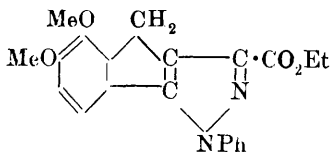
4:5-Dimethoxy-1-hydrindone, yellow leaflets, m. p. 77—78° (Perkin and Robinson, T., 1914, 105, 2388, give 82°), is conveniently prepared from 2:3-dimethoxy- $\beta$ -phenylpropionic acid by the successive action of phosphorus pentachloride and aluminium chloride. Attempts to convert it into an azomethine by the action of *p*-nitrodimethylaniline and potassium hydroxide were unsuccessful, the alkali affecting almost exclusively the nitroso-base and forming *pp'*-tetramethyldiaminoazoxybenzene, yellowish-brown needles, m. p. 239—240°. 4:5-Dimethoxy-2-hydroxymethylene-1-hydrindone, almost colourless needles, m. p. 135—136°, after softening at 130°, is prepared by the action of sodium and ethyl formate on the hydrindone; the *copper* salt, greenish-yellow powder, and the *anilide*,  $C_{11}H_{10}O_3 \cdot CH \cdot NHPh$ , yellow prisms, m. p. 168°, are described.



When the hydroxymethylene compound is heated at 160° it loses formic acid and yields a compound (annexed formula), red prisms, m. p. 222°.

Ethyl oxalate condenses with 4:5-dimethoxy-1-hydrindone in the presence of sodium ethoxide, yielding *ethyl* 4:5-dimethoxy-1-

*hydrindoneglyoxylate*, yellow needles, m. p. 132—133°, from which



the corresponding *acid*, yellow needles, m. p. 232°, is obtained in the usual manner. The ester reacts readily with phenylhydrazine hydrochloride in the presence of a few drops of concentrated hydrochloric acid, giving *ethyl 7:8-dimethoxy-1-phenylindeno-2' : 3' : 4 : 5-pyr-*

*azole-3-carboxylate* (annexed formula), colourless, silky needles, m. p. 172—173°; the corresponding acid forms slender needles, m. p. 240—241° (decomp.). H. W.

**Ethyl Diphenyleneacetate.** S. RUHEMANN (*Ber.*, 1920, **53**, [B], 287—289).—The sodio-derivative of ethyl fluorene-9-dicarboxylate (Wislicenus and Mocker, A., 1913, i, 1187) reacts with ethyl phenylpropionate to yield carbon dioxide and *ethyl β-diphenylenemethylcinnamate*,  $\begin{matrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{matrix} > \text{CH} \cdot \text{CPh} \cdot \text{CH} \cdot \text{CO}_2\text{Et}$ , yellow crystals, m. p.

98—99°; the corresponding *acid* crystallises in yellow leaflets, m. p. 219—220°, and is reduced by sodium amalgam to *β-diphenylene-methyl-β-phenylpropionic acid*, colourless prisms, m. p. 184—185°.

H. W.

### Regularities Observed in the Pyrogenic Degradation of certain Cyclic Hydroxy-acids of the Benzene Series.

HERMANN KUNZ-KRAUSE and PAUL MANICKE (*Ber.*, 1920, **53**, [B], 190—201).—When salicylic acid is rapidly heated to a temperature not exceeding 250°, it loses carbon dioxide and water, but only 46.39% of it is converted into phenyl salicylate; at temperatures between 250° and 350°, carbon dioxide is evolved in regularly increasing amount, and, above 280°, the formation of phenol in small quantity can be detected. When rapidly distilled, the acid (contrary to the generally accepted views) does not undergo an even partial, smooth conversion into carbon dioxide and phenol; the product only contains very small quantities of the latter in addition to salol and other substances. Similar experiments with protocatechuic acid (3:4-dihydroxybenzoic acid) show that a smooth decomposition into catechol and carbon dioxide does not occur between 200° and 300°. Rapid distillation of protocatechuic acid yields carbon dioxide, catechol, and tetrahydroxyanthraquinone (rufiopine). Gallic acid, on the other hand, is quantitatively converted at 240—245° into carbon dioxide and pyrogallol or Pelouze's melan-gallic acid; when rapidly distilled it yields 1:2:3:5:6:7-hexahydroxyanthraquinone. The formation of derivatives of anthracene from benzene compounds by a purely pyrogenic action is of interest in that it affords a possible explanation of the occurrence of compounds of the two series in coal tar. H. W.

### Syntheses of Naphthyl-lactic and Naphthylcinnamic Acids.

**II. β-Phenyl-β-2-naphthyl-lactic Acid.** REMO DE FAZI (*Gazzetta*, 1919, **49**, ii, 250—253. Compare A., 1919, i, 529).—β-Phenyl-β-2-

*naphthyl-lactic acid*,  $C_{10}H_7 \cdot CPh(OH) \cdot CH_2 \cdot CO_2H$ , obtained as ethyl ester by decomposing by means of acidified water the complex formed by the interaction of phenyl  $\beta$ -naphthyl ketone and ethyl bromoacetate in benzene solution in presence of zinc dust, forms slender, white needles, m. p. 225—226°, and with concentrated sulphuric acid gives an emerald-green coloration, which immediately changes to yellowish-brown with intense green fluorescence. The *ethyl* ester forms white laminæ, m. p. 114—115°, and with concentrated sulphuric acid gives an intensely green solution showing marked green fluorescence.

T. H. P.

**Phthaleins and Fluorans.** MAURICE COPISAROW (T., 1920, 117, 209—218).

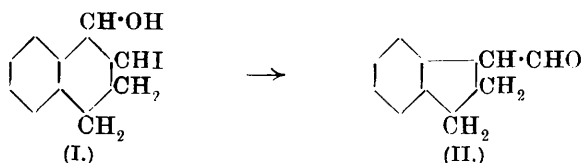
**Preparation of *p*-Dimethylaminobenzaldehyde.** T. INGVALDSEN and L. BAUMAN (*J. Biol. Chem.*, 1920, 41, 145—146).—The authors modify the method of Ullmann and Frey (A., 1904, i, 423) by omitting the isolation of the hydrochloride of the benzylidene compound prepared by the condensation of *p*-nitrosodimethylaniline and *p*-dimethylaminobenzyl alcohol, and decomposing the free base by formaldehyde and acetic acid at the ordinary temperature. The crude aldehyde is purified by distillation in a partial vacuum.

J. C. D.

**The Iodhydrin Derived from Cinnamyl Methyl Ether.** HENRI BEAUFOUR (*Bull. Soc. chim.*, 1920, [iv], 27, 148—152. Compare A., 1912, i, 621; 1913, i, 466, 467).—The iodohydrin obtained by treating cinnamyl methyl ether with iodine and mercuric oxide (*loc. cit.*), when slowly added in ethereal solution to an aqueous solution of silver nitrate (compare Tiffeneau. A., 1907, i, 922), give *methyltropaldehyde*,  $OMe \cdot CH_2 \cdot CHPh \cdot CHO$ , b. p. 217—218°,  $D_0$  1.0711, giving an *oxime*, b. p. 175°/15 mm.,  $D_0$  1.121, and a *semi-carbazone*, m. p. 125°. On oxidation it yields *methyltropic acid*, m. p. 63°, b. p. 177—180°/15 mm., giving an *ethyl* ester, b. p. 139—140°/10 mm. or 250—251°/765 mm.,  $D_0$  1.0724. Attempts to prepare the corresponding primary alcohol by reduction of this ester were not successful, the main product, in every case, being atropic acid.

W. G.

**Phenylic Transposition in the Tetrahydronaphthalene Series.** M. TIFFENEAU and A. ORÉKHOFF (*Compt. rend.*, 1920, 170, 465—467).—The iodohydrin of  $\alpha\beta$ -tetrahydronaphthalene glycol (I), when treated with silver nitrate in ethereal solution undergoes phenylic transposition, giving *hydrindene-2-aldehyde*



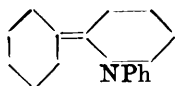
(formula II), b. p.  $135^{\circ}/30$  mm.,  $D_0^{20}$  1.095, giving a *semicarbazone*, m. p.  $167^{\circ}$ , an *oxime*, m. p.  $104^{\circ}$ , and a *bisulphite* compound.

Neither the iodhydrin of  $\beta\beta$ -tetrahydronaphthalene glycol nor the iodhydrin of hydrindene glycol undergoes this transposition when similarly treated with silver nitrate. W. G.

**The Beckmann Rearrangement. IX. Action of Phosphorus Pentasulphide on Benzophenoneoxime.** MITSURU KUHARA and Kôzô KASHIMA (*Mem. Coll. Sci. Kyoto Imp. Univ.*, 1919, **4**, 69—75. Compare A., 1918, i, 179).—Dodge (A., 1891, 1238) and Ciusa (A., 1906, i, 953) have observed that thiobenzanilide is formed when benzophenoneoxime is warmed with phosphorus pentasulphide, and have ascribed this change to the Beckmann rearrangement of thiobenzophenoneoxime, formed according to the equation  $5\text{CPh}_2\cdot\text{N}\cdot\text{OH} + \text{P}_2\text{S}_5 = 5\text{CPh}_2\cdot\text{N}\cdot\text{SH} + \text{P}_2\text{O}_5$ . In analogy with Kuhara's previous studies of this transformation, it is now found that the rearrangement is due to the formation of an ester of the thio-oxime, for when the reaction is carried out in ethereal suspension, *thiobenzophenoneoxime hydrogen phosphate*,  $\text{OH}\cdot\text{PO}(\text{SN}\cdot\text{CPh}_2)_2$ , is obtained as a fibrous, greenish-yellow mass, which changes into thiobenzanilide with almost explosive violence at  $70^{\circ}$ . A more stable derivative is obtained by treating this ester with cold, alcoholic potassium hydroxide, the product being *thiobenzophenoneoxime dipotassium hydrogen orthophosphate*,  $\text{OH}\cdot\text{PO}(\text{OK})_2(\text{SN}\cdot\text{CPh}_2)_2$ , a white, crystalline powder which changes into thiobenzanilide at  $149^{\circ}$ . J. C. W.

**Zinc Chloride as a Condensing Agent. V. Condensation Products of Aniline and Hydroaromatic Ketones.** G. REDDELIEN and O. MEYN (*Ber.*, 1920, **53**, [B], 345—354. Compare A., 1914, i, 698, and following abstract).—It has been shown previously that aniline zincchloride powerfully catalyses the condensation of ketones with amines, and is the only useful agent in the cases of enolisable ketones containing the group  $\cdot\text{CO}\cdot\text{CH}_2\cdot$  and of unsaturated ketones of the type  $>\text{C}:\text{C}:\text{CO}$ . It is now found to be applicable to hydroaromatic ketones.

*cycloHexanoneanil*, pale yellow oil. b. p.  $140^{\circ}/19$  mm., is obtained by heating *cyclohexanone*, aniline, and aniline zincchloride at  $155^{\circ}$  during twenty minutes; with other condensing agents, such as aniline hydrochloride, extensive auto-condensation and considerable resinification take place, and non-uniform products of very high boiling point are formed. *cycloHexanoneanil* is a reactive substance which undergoes auto-condensation, yielding the *substance*,  $\text{C}_{18}\text{H}_{23}\text{N}$ , b. p.  $212\text{—}214^{\circ}/18$  mm., which is regarded as *cyclohexylidene-2-cyclohexanoneanil* (annexed formula), since, when treated with dilute acids, it gives aniline and *cyclohexylidene-2-cyclohexanone* (compare Wallach, A., 1907, i, 220; Manich, A., 1907, i, 205). The condensed anil is the main product of the action of aniline on *cyclohexanone* in the presence of aniline



zincichloride at  $180^{\circ}$  for three-quarters of an hour, and can also be prepared by heating *cyclohexanoneanil* with aniline hydrochloride for a few minutes at  $200^{\circ}$ . At a higher temperature it also undergoes auto-condensation, and yields aniline and an *anil*, possibly  $C_{18}H_{26}NPh$ , dark yellow oil, b. p.  $240-250^{\circ}/14$  mm.

Similarly, menthone yields *menthoneanil*, yellow oil, b. p.  $159-160^{\circ}/12$  mm.; *menthone-p-toluil*, yellow oil, b. p.  $178^{\circ}/16$  mm.; and *menthone-p-anisil*, colourless crystals, m. p.  $61.5^{\circ}$ , b. p.  $195^{\circ}/16$  mm. These substances cannot be preserved for any length of time in contact with air, since they become oxidised and darken in colour. Condensing agents other than aniline zincichloride yield dark brown, resinous oils.

Among unsaturated hydroaromatic ketones, pulegone yields a normal *anil*, yellow oil, b. p.  $148-152^{\circ}/12$  mm., and, in addition, *7-anilinomenthone*, b. p.  $154-158^{\circ}/13$  mm., and *7-anilinomenthoneanil*, b. p.  $153-156^{\circ}/18$  mm.; the latter substances are probably formed by simple addition of aniline to pulegone and pulegone-anil respectively by a process which is not infrequently associated with the action of amines on substances having conjugated double bonds. Dihydrocarvone, on the other hand, yields the *anil*, yellow oil, b. p.  $170-171^{\circ}$ , very smoothly and without noticeable formation of by-products. *Carvoneanil*, pale yellow oil, b. p.  $180-182^{\circ}/17$  mm., is remarkably readily prepared, reaction occurring to some extent between the components at  $160^{\circ}$  in the absence of catalyst. Camphor, on the other hand, did not react with aniline itself, and only to a small extent in the presence of aniline zincichloride; *camphoranil*, yellow oil, b. p.  $164.5-166^{\circ}/15$  mm., m. p.  $13.5^{\circ}$ , could be obtained in 64% yield by the use of aniline hydrochloride as condensing agent.

Solution of the anils of the unsaturated hydroaromatic ketones in concentrated sulphuric acid gives an intense blue coloration with nitric acid. The reaction is as sensitive as the brucine test. It is shown by carvoneanil, pulegoneanil, and dihydrocarvoneanil (in order of decreasing sensitiveness), but not by *cyclohexanoneanil*, menthoneanil, or camphoranil. The action thus appears to depend on the presence of the group  $>C:C:C:NPh$ . The presence of the anil group is shown to be essential, since the coloration is not given by carvonephenylhydrazone. Nitrite, chlorate, chromate, and hydrogen peroxide also yield the colour, which therefore depends on oxidation.

H. W.

**Condensation Products from Benzylamine and Aromatic Ketones.** G. REDDELIEN (*Ber.*, 1920, **53**, [B], 334-340).—It has been shown previously (A., 1913, i, 1203) that hydrogen haloids are frequently effective catalysts in promoting the action of aromatic ketones with amines to form ketoneanils; it is now shown that benzophenonebenzylimide,  $CPh_2:N\cdot CH_2Ph$ , m. p.  $60-61^{\circ}$ , is readily obtained from benzophenone and benzylamine at  $180^{\circ}$  in the presence of a few drops of hydrobromic acid solution; Hantzsch and Hornbostel (A., 1898, i, 195) have previously prepared the same

substance from benzophenone dichloride, since they found that the ketone and amine did not react to an appreciable extent with one another even at an elevated temperature. Acetophenonebenzylimide, transparent needles, m. p.  $44.5^{\circ}$ , can be obtained in improved yield from the ketone and amine by a slight modification of the procedure of Hantzsch and Hornbostel (*loc. cit.*); when, however, the condensation is effected in the presence of  $\text{ZnCl}_2, 2\text{NH}_3$  or hydrobromic acid an entirely different substance is obtained, which is identified as 2:4:6-triphenylpyridine, and is shown to be identical with the product prepared from benzylidenediacetophenone and hydroxylamine by Wislicenus and Newmann (A., 1899, i, 61), from acetophenone and ammonia in the presence of phosphoric oxide (Engler and Heine, this Journ., 1873, 1036; Riehm, A., 1887, 599), and by the distillation of acetophenone ammonia (Thomas, A., 1907, i, 138). The substance behaves as a very feeble base, but, when crystallised from concentrated hydrochloric acid, gives a *hydrochloride*, which somewhat rapidly loses hydrogen chloride when preserved; it separates as unchanged base from its solution in more dilute acid. The formation of triphenylpyridine from acetophenonebenzylimide is accompanied by that of benzylamine or dibenzylamine and methane.

H. W.

### Catalytic Action of Hydrogen Haloids in Condensations.

**II. The Decomposition of Anils.** G. REDDELIEN (*Ber.*, 1920, 53, [B], 355—358).—It has been shown previously (A., 1913, i, 1203) that hydrogen haloids are effective catalysts in the formation of anils from ketones and aniline, and emphasis has been laid on the necessity of a vigilant control of the temperature of the reaction if the formation of by-products in large amounts is to be avoided. Further investigation now shows that the anils are decomposed when heated with aniline hydrobromide. Thus, benzylideneaniline, when distilled with the addition of a small quantity of dry aniline hydrobromide, gave aniline, toluene, and acridine, in addition to much brown, resinous matter. A somewhat similar behaviour was observed with fluorenoneanil and benzildianil, which evolved aniline at above  $200^{\circ}$ ; benzophenoneanil, on the other hand, appeared to be stable.

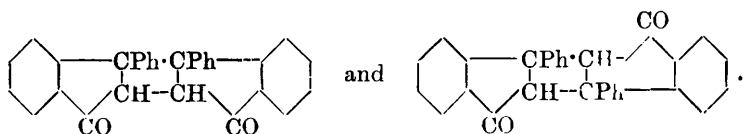
The possibility of utilising the elimination of aniline for the condensation of anils with reactive hydrocarbons has also been investigated. Benzophenoneanil and diphenylmethane scarcely reacted with one another. Benzophenoneanil and fluorene did not react below  $300^{\circ}$ , but, after addition of a small quantity of aniline hydrobromide, aniline was readily evolved at  $270^{\circ}$ , and a hydrocarbon was obtained which was identified as bisdiphenylene-ethane instead of the expected diphenyldiphenylene-ethylene, whilst bisdiphenylene-ethylene was also formed in minor quantity. Fluorenoneanil and fluorene yielded a similar mixture of hydrocarbons.

H. W.

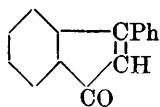
### Indones. III. 3-Phenylindone and Diphenyltruxones.

REMO DE FAZI (*Gazzetta*, 1919, 49, ii, 253—263. Compare A., 1915, i, 1063; 1916, i, 151).— $\beta\beta$ -Diphenyl-lactic acid does not give

3-phenylindone when treated with phosphoric oxide, but its ethyl ester yields with sulphuric acid the emerald-green coloration regarded by the author as characteristic of those derivatives of lactic and cinnamic acids which are capable of furnishing indones. The green solution is found to contain: (1) a small proportion of an orange-red compound which, in acetic acid solution containing palladium-black, absorbs hydrogen forming 3-phenylhydrindone, and must therefore be 3-phenylindone; (2) considerable proportions of two colourless compounds,  $C_{30}H_{20}O_2$ , which are dimerides of 3-phenylindone, do not combine with chlorine or bromine, and give no coloration with sulphuric acid; they are therefore regarded as isomeric diphenyltruxones (compare Liebermann, A., 1898, i, 662), having the probable constitutions:



3-Phenylindone (annexed formula) forms an orange-red powder, m. p. 69—71°, and gives an emerald-green coloration with sulphuric acid.

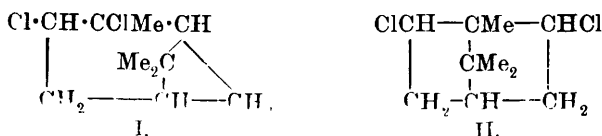


The two *diphenyltruxones* form (1) large, cubical crystals, m. p. 252—253°, and (2) shining, transparent, white prisms, m. p. 209—211°. Both have the normal molecular weights in boiling chloroform.

In acetic acid or alcoholic solution, isomeride (2) does not absorb hydrogen in presence of palladium-black, but in acetic acid isomeride (1) slowly absorbs hydrogen, giving a *compound*,  $C_{30}H_{24}O_2$ , which forms shining, white scales and does not melt at 275°; in this compound the two carbonyl groups of the diphenyltruxone are converted into  $CH(OH)$  groups. T. H. P.

**Some Derivatives of Fisetol.** WILLIAM KERSHAW SLATER and HENRY STEPHEN (T., 1920, 117, 309—319).

**Chlorination of Pinene.** OSSIAN ASCHAN (*Öfvers. Finska Vet. Soc.*, 1915, 57, 14 pp.; from *Chem. Zentr.*, 1918, ii, 952—953).—The chlorination of pinene in the absence of moisture at  $-15^\circ$  to  $0^\circ$  has been investigated; the results differ from any previously recorded. Chlorination occurs in a highly complex manner. The first fractions of the product give abundant solid deposits of pinene hydrochloride. From the higher fractions only a *pinene dichloride* (? II) was obtained, which may have been formed from a primary,



m\*



normally formed, unstable dichloro-additive compound (I). It forms transparent, rhombic, bipyramidal, plate-like crystals, m. p. 173—174°, b. p. ca. 130°/10 mm. In addition, a liquid dichloride, b. p. ca. 120—125°/10 mm., which could not be isolated in the pure condition, is also produced. Neither dichloride is affected by boiling aniline.

Preliminary experiments show that pinene hydrochloride can be readily chlorinated in chloroform or carbon tetrachloride solution until four additional atoms of hydrogen have been replaced. Colourless, crystalline products, m. p.'s 135°, 150—152°, and 130° respectively, have thus been obtained, analyses of which give results intermediate between those required for  $C_{10}H_{15}Cl_3$  and  $C_{10}H_{14}Cl_4$ ; the formation of a dichloride was not observed. H. W.

**The Relative Power of Addition of Unsaturated Compounds.** OSSIAN ASCHAN (*Öfvers. Finska Vet. Soc.*, 1916, 58, 9 pp.; from *Chem. Zentr.*, 1919, ii, 953).—The action of pinene on different terpene hydrochlorides, particularly at elevated temperature, regularly occurs in such a manner that hydrogen chloride is withdrawn from the latter and ordinary pinene hydrochloride (bornyl chloride) is produced; this is demonstrated in the cases of dipentene dihydrochloride, sylvestrene dihydrochloride, camphene hydrochloride, and dipentene monohydrochloride. Pinene can even remove hydrogen chloride slowly from dry aniline hydrochloride or ammonium chloride. Nopinene and the bicyclic terpene, b. p. 163—165°, recently isolated from Finnish oil of turpentine and provisionally termed  $\gamma$ -pinene, behave similarly to ordinary pinene. In like manner, hydrogen bromide is removed by pinene from camphene hydrobromide or dipentene dihydrobromide. When heated with aniline sulphate and acetic acid, pinene gives isobornyl acetate. On account of its unsaturated nature, pinene behaves in this respect as a base. Even with complex halogen additive products, such as dipentene tetrabromide, pinene effects the removal of halogen acid. This behaviour of pinene and analogous substances is probably attributable to the relatively great latent heat of these terpenes. H. W.

**Preparation of Organic Camphol Esters and of Borneol from them in the Presence of Sulphoricinic Acid, which Acts as a Solvent for Camphene or Pinene Hydrochloride.** ANDRÉ DUBOSC (*Caoutchouc et Guttapercha*, 1918, 15, 9555; from *Chem. Zentr.*, 1920, i, 115).—The difficulty of preparing organic camphol esters lies, in part, in the sparing solubility of the substances to be esterified in the acids used; it is now shown that solution can be effected by the addition of sulpho-compounds, particularly of sulphoricinic acid, and that these do not take further part in the action. The separation of ester from sulphoricinic acid and from excess of the acid under esterification occurs in the usual manner. The corresponding camphor alcohols may be obtained by hydrolysis of the esters. H. W.

**New Hydrocarbons of High Molecular Weight from Isoprene.** OSSIAN ASCHAN (*Öfvers. Finska Vet. Soc.*, 1916, 58, 42 pp.; from *Chem. Zentr.*, 1918, ii, 954—955).—The additive capacity of caoutchouc shows that one double bond of isoprene disappears in its formation, and is utilised in uniting the condensed isoprene molecules. The molecules which are thus formed by purely chemical reaction are subsequently united to greater complexes, probably by physical and secondary chemical forces (such as residual affinities). According to the author, therefore, two processes are operative in the formation of caoutchouc, which differ from one another not only in respect of rapidity, but also of nature, namely, first, a purely chemical condensation involving certain ethylenic bonds in isoprene and leading to new carbon compounds, and, secondly, formation of greater complexes from the "simplest caoutchouc molecules" so formed which does not involve the production of carbon compounds in the ordinary sense. The latter process only takes place gradually, and is probably never complete; it constitutes the so-called polymerisation of caoutchouc. The converse process, depolymerisation, occurs when caoutchouc forms additive products and when it is dissolved, particularly in hot solvents.

The properties of caoutchouc tetrabromide show it to have a molecular weight which cannot be estimated by the ebullioscopic method. The formation of the complex molecule cannot, however, be a subsequent operation, since the additive product is itself saturated. Bromine is added at the double bonds which remain after or are formed during the polymerisation of isoprene, and in proportion as addition proceeds at the "simplest caoutchouc molecules" the powers of complex formation, present in the caoutchouc, are placed out of action; the state of division of the substance probably remains at the stage corresponding with the "simplest caoutchouc molecules." According to this view, the molecules of caoutchouc and its bromide are both large, but of different orders of magnitude. The tetrabromide is therefore actually amorphous, but has not the viscous consistency of caoutchouc, which indicates a very high molecular weight. The same may be said for most of the other additive products of rubber. In experimental confirmation of the view that the synthesis of caoutchouc takes place in two stages, it is shown that isoprene condenses with other hydrocarbons containing an ethylenic linking, such as amylene ( $\beta$ -methyl- $\Delta^2$ -butylene), pinene, camphene, and with itself, yielding compounds of very high molecular weight which are amorphous, but do not possess the physical properties of caoutchouc. Both the course of the reaction and the mode of action of the necessary catalyst ( $\text{AlCl}_3$ ) indicate that the process is one of actual condensation which proceeds to completion. The products are still unsaturated, but add much less bromine than does caoutchouc. Two different classes of compounds are invariably formed, both of which are solid, but of which the one (*A* product) is completely insoluble in all solvents, whilst the other (*B* product) dissolves in most organic media with

the exception of alcohol. Isomerism probably depends on difference in molecular weight.

A large number of individual experiments are described in the original which do not lend themselves to abstraction. Commercial isoprene yields two different *products* with aluminium chloride; both have the composition  $(C_{10}H_{18})_n$ , but, as was found subsequently, the nature varies with differing proportions of isoprene and amylene. The consecutive products obtained by the step-wise condensation with aluminium chloride have the same percentage composition. Soluble and insoluble substances are alike unsaturated, and have almost identical additive powers. Pure isoprene and pure  $\beta$ -methyl- $\Delta^{\beta}$ -butylene, when separately treated with aluminium chloride, give products of a completely different type. Experiments with mixtures of the two showed that practically only the isoprene of the mixture was acted on if the proportion of amylene was small and the action was cautiously performed. The condensation products must therefore be regarded as polymerised isoprenes. They are not identical, but isomeric, with caoutchouc. Oily substances are obtained as by-products of these condensations, which are possibly synthetic hydrocarbons of the sesqui-, di-, and poly-terpene series. It is further shown that isoprene can be condensed with pinene and camphor to products similar to those formed with  $\beta$ -methyl- $\Delta^{\beta}$ -butylene; it condenses, in addition, with isopinene, dipentene, and sylvestrene.

H. W.

**Digitalis Substances. XL.** H. KILIANI (*Ber.*, 1920, 53, [B], 240—250).—In a previous communication (*A.*, 1919, i, 214), the author has described the degradation of digitogenic acid into a lactone,  $C_8H_{12}O_2$ , and a monobasic acid. Further examination of the former and the preparation of an *acetyl* derivative, m. p. 89—90°, lead to the adoption of the formula  $C_{12}H_{18}O_3$ , and this is confirmed by a study of the *magnesium* salt of the corresponding acid. It is also found that the lactone contains 10—15% of a *substance*,  $C_{12}H_{18}O_3$ , m. p. 76°, which is not dissolved by boiling dilute aqueous alkali, and that the lactone cannot be recovered as such from its solutions in alkali. Revision of the formula of the lactone necessitates alteration in that of the monobasic acid, which should have the composition  $C_{16}H_{26}O_5$ ; re-examination of the product shows that it is not homogeneous, but contains ethyl hydrogen digitogenate, after removal of which, however, the acid still does not conform to the expected formula.

Digitaligenin has  $[\alpha]_D + 454^\circ$  in 95% alcohol,  $+ 443^\circ$  in alcohol, whilst the hydro-product (*A.*, 1919, i. 91) has  $[\alpha]_D + 42^\circ$  in 95% alcohol; contrary to the previous statement, the latter yields only a monoacetyl derivative, m. p. 165°. Digitaligenin is converted by formic acid in the presence of sodium formate into a *monoformyl* derivative, leaflets, m. p. 169°; and is not hydrolysed by treatment with hot dilute alcoholic hydrochloric acid.

Digitoxigenin is not hydrolysed by 2% hydrochloric acid, but is converted into a *substance*,  $C_{22}H_{32}O_4$ , m. p. 175°; *acetyldigitoxigenin*

forms short, coarse rods, m. p. 211—212°. Cautious oxidation of digitoxigenin by chromic acid converts it into a crystalline substance,  $C_{19}H_{26}O_4$ , which is converted by alcoholic hydrochloric acid into toxigenone, m. p. 260°; the latter is slowly transformed by hot alcoholic sodium hydroxide solution into an amorphous sodium derivative, and hence, contrary to previous statements, appears to have lactonic character.

Sodium dixgeninate is oxidised by cold potassium permanganate solution, yielding an *acid*,  $C_{17}H_{24}O_6 \cdot 1.5H_2O$ , platelets, m. p. 218—219°,  $[\alpha]_D -31.4^\circ$ , as potassium salt (the *calcium* salt,  $C_{17}H_{12}O_6Ca \cdot 1.5H_2O$  was analysed); the acid is not affected by an excess of hot sodium hydroxide solution or by cold permanganate, and only slowly by hot permanganate. On the other hand, it is very susceptible to hot hydrochloric acid, which converts it into an *acid*, needles, m. p. 120°, equivalent ca. 300. It is converted by nitric acid into an *acid*, which becomes discoloured at 235° and has m. p. 270° (decomp.); the *calcium* salt was analysed. The investigation of these acids is not yet complete.

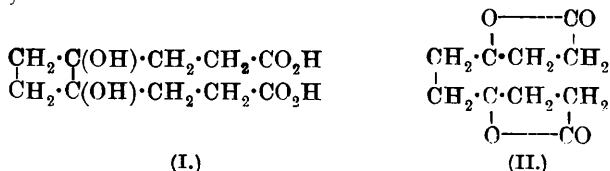
H. W.

### A New Glucoside Hydrolysable by Emulsin: Scabiosin.

EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1920, **170**, 486—491).—The roots of *Scabiosa succisa*, L., contain sucrose, obtainable in a crystalline form, and also a new glucoside, *scabiosin*.  $[\alpha]_D -106.52^\circ$ , which, when hydrolysed by emulsin or by dilute sulphuric acid, gives dextrose and a yellow substance insoluble in water.

W. G.

**Tetrahydroanemonin.** Y. ASAHINA and M. ATSUMI (*J. Pharm. Chim.*, 1920, [vii], **21**, 135—136).—Tetrahydroanemonin,  $C_{10}H_{12}O_4$ , when treated with sodium ethoxide in alcoholic solution, gives a *sodium* salt,  $C_{10}H_{14}O_6Na_2$ , very soluble in water, and no longer possessing the ketonic function of anemonin. When acidified, the sodium salt gives, not an acid, but tetrahydroanemonin, which therefore seems to be the dilactone of an unstable acid. The constitutions assigned to this acid and the tetrahydroanemonin are given by formulæ I and II:



The sodium salt, on oxidation in neutral solution with potassium permanganate, yields the sodium salt of anemononic acid.  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ .

W. G.

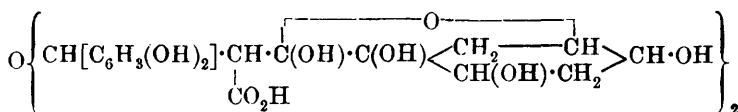
### Use of Butyl Alcohol as a Solvent for Anthocyanins.

OTTO ROSENHEIM (*Biochem. J.*, 1920, **14**, 73—74).—Butyl alcohol removes all the anthocyanins from their solutions in dilute acids. Comparative tests show that the monoglucosides, chrysanthemin

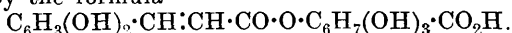
and oenin, are four times as soluble in butyl alcohol as in amyl alcohol; idaein is ten times as soluble. Of the rhamno-glucosides, prunicyanin is sixteen times as soluble, and violanin is twenty-five times as soluble, as in amyl alcohol. Butyl alcohol, therefore, is a suitable solvent for use in the preparation of these substances in the pure condition. The author has prepared pure specimens of oenin from grapes and pure idaein from cranberries by means of this solvent.

J. F. S.

**Tannins. III. Chlorogenic Acid, the Tannin-like Constituent of Coffee.** KARL FREUDENBERG (*Ber.*, 1920, 53, [B], 232—239).—Chlorogenic acid has been extensively investigated by Gorter (*A.*, 1911, i, 221, and previous abstracts), who has assigned to it the annexed formula:



This is not easily reconciled with the production of caffeic acid from it under the influence of *Mucor* or *Penicillium* varieties. Repetition of the fission experiments, using tannase, has shown that chlorogenic acid yields caffeic and quinic acids. It has also been found that chlorogenic acid, which Gorter considered to be anhydrous, actually contains  $\frac{1}{2}\text{H}_2\text{O}$ ; this accounts for the difference between it and the hypothetical hemichlorogenic acid. Chlorogenic acid thus appears simply as a depside of caffeic and quinic acids, and, as appears from Gorter's experiments, the carboxy-group of caffeic acid is united to a hydroxy-group of quinic acid, as indicated by the formula

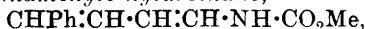


H. W.

**The Action of Sodium Hypochlorite on Amides.** I. J. RINKES (*Rec. trav. chim.*, 1920, 39, 200—207).—Sodium hypochlorite acts on  $\alpha\beta$ -unsaturated amides in the presence of methyl alcohol to give urethanes, which, when hydrolysed with dilute sulphuric acid, yield saturated aldehydes, containing one atom less of carbon than the original amide.

Furylacrylamide,  $\text{C}_4\text{H}_3\text{O} \cdot \text{CH} \cdot \text{CH} \cdot \text{CO} \cdot \text{NH}_2$ , under these conditions yields *furylvinylurethane*,  $\text{C}_4\text{H}_3\text{O} \cdot \text{CH} \cdot \text{CH} \cdot \text{NH} \cdot \text{CO}_2\text{Me}$ , m. p.  $102^\circ$ , which on hydrolysis gives *furylacetaldehyde*,  $\text{C}_4\text{H}_3\text{O} \cdot \text{CH}_2 \cdot \text{CHO}$ , giving a *p*-nitrophenylhydrazone, m. p.  $126^\circ$ , and a *semicarbazone*, m. p.  $130^\circ$ .

Cinnamaldehyde condenses with cyanoacetic acid to give  $\alpha$ -cyano-cinnamenylacrylic acid, which, when heated with copper powder, yields cinnamenylacrylonitrile, and this when allowed to remain in contact with fuming hydrochloric acid and ether, gives cinnamenylacrylamide. This amide, with sodium hypochlorite and methyl alcohol, yields *cinnamenylvinylurethane*,



m. p. 134—135°, which is hydrolysed by sulphuric acid to  $\beta$ -benzylidenepropaldehyde,  $\text{CHPh}:\text{CH}\cdot\text{CH}_2\cdot\text{CHO}$ , giving a *p*-nitrophenylhydrazone, a semicarbazone, m. p. 192° (decomp.), and an oxime, m. p. 117°.

W. G.

### Pyrylium Compounds. VI. Quino-pyran Derivatives.

W. DILTHEY and R. TAUCHER (*Ber.*, 1920, **53**, [B], 252—260).—In extension of the work of Dilthey (*A.*, 1919, i, 413), pyrylium salts having a methoxy- or hydroxy-group in the *para*-position in the phenyl group in position "4" have now been prepared which are found to be closely analogous to the corresponding salts in which the  $\alpha$ -phenyl group is similarly substituted.

*Anisylidenediacetophenone*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{CH}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_5)_2$ , colourless, coarse crystals, m. p. 105°, is prepared by the condensation of anisaldehyde and acetophenone with sodium hydroxide in boiling aqueous alcoholic solution; a second *modification*, long, shining crystals, m. p. 93°, is also described, which passes into the former when crystallised from benzene. The *disemicarbazone* forms colourless crystals, m. p. 246—247°. Anisylidenediacetophenone (or a mixture of anisylideneacetophenone and acetophenone) is converted by hydrated ferric chloride in acetic anhydride solution into

the iron salt of 2:6-diphenyl-4-*p*-anisylpyrylium chloride (annexed formula), small, yellow needles, m. p. 226°, which is transformed by sodium acetate

in dilute aqueous solution into  $\alpha$ -hydroxy- $\epsilon$ -keto- $\alpha$ -diphenyl- $\gamma$ -*p*-anisyl- $\Delta^{\alpha\gamma}$ -pentadiene,  $\text{OH}\cdot\text{CPh}:\text{CH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})\cdot\text{CH}\cdot\text{COPh}$ , slender needles, m. p. 122° (*disemicarbazone*, colourless crystals, m. p. 218°; *picrate*, reddish-brown needles, m. p. 244°; *acid hydrochloride*, yellow, crystalline precipitate, which decomposes at about 140°). Demethylation of the *pseudo*-base with concentrated hydrochloric acid at 160—170° gives 2:6-diphenyl-4-*p*-hydroxyphenylpyrylium hydrochloride, steel-blue, shining needles, m. p. 320°, after slowly changing from 235° (an *acid chloride*,  $\text{C}_{23}\text{H}_{17}\text{O}_2\text{Cl}\cdot 0\cdot 5\text{HCl}$ , yellow crystals, is also described); demethylation with hydrobromic acid gives the corresponding *bromide*, brownish-red crystals, m. p. above 320°, which appears to exhibit little tendency towards further combination with the halogen acid. The chloride is converted by water and a slight excess of sodium acetate into 2:6-diphenyl-4-quino-

pyran,  $\text{O}\langle\text{CPh}:\text{CH}\rangle\text{C}:\text{C}_6\text{H}_4:\text{O}$ , dark red crystals with a bronze

glance, m. p. 262—264°; the anhydro-base is almost instantaneously decolorised by semicarbazide, but does not yield a semicarbazone. Addition of water to the anhydro-base occurs less readily than with the  $\alpha$ -isomeride, and is best effected by cautious addition of water to the alcoholic solution, whereby the *carbinol* base,  $\text{O}\langle\text{CPh}:\text{CH}\rangle\text{C}\langle\text{OH}\rangle\text{C}_6\text{H}_4\cdot\text{OH}$ , is precipitated in pale red crystals.

It is much less stable than the corresponding  $\alpha$ -derivative, and

readily loses water when heated, and re-forms the pseudo-base. It is more readily isolated as its *monoacetyl* derivative, pale yellow, silky needles, m. p. 122—123°.

Prolonged action of pyridine on the demethylated chloride leads to the formation of two *substances*,  $C_{23}H_{20}O_4$ , needles, m. p. 166°, and  $C_{23}H_{20}O_6$ , colourless crystals, m. p. 239—240°, respectively. These compounds do not exhibit any relationship to the red anhydro-base, and are probably formed by fission of the ring.

[*Addendum to Part IV.*—W. DILTHEY.]—The *disemicarbazone* of  $\alpha$ -hydroxy- $\epsilon$ -keto- $\gamma\epsilon$ -diphenyl- $\alpha$ -p-hydroxyphenyl- $\Delta^{\gamma}$ -pentadiene forms colourless, transparent prisms, m. p. 191—192°. The acid picrate of 2:6-diphenyl-4-*p*-anisylpyrylium, m. p. 237—238° (A., 1919, i, 413) is now found to have a normal constitution. H. W.

### Pyrylium Compounds. VII. Carbonium or Oxonium?

WALTHER DILTHEY (*Ber.*, 1920, 53, [B], 261—265).—The author is led to reject the carbonium formula for pyrylium compounds, since several basic carbon atoms must be taken into consideration, and thus there is no possibility of a uniform conception. For a similar reason, the oxonium formula is rejected. Regarding the basic properties of oxygen as proved, there would be in the pyrylium salts three carbon atoms and two oxygen atoms to which negative radicles might be attached, whilst it is also possible that the para-carbon atom of the phenyl residue can function in the formation of salts. In proportion as the number of basic atoms in the molecule increases, it becomes more certain that no single one of them is united to the negative group, and more probable that the latter is attached to the molecule as a whole. A somewhat similar idea has been advanced by Kauffmann (this vol., i, 50), who, however, regards the cationic partial valencies as associated with definite atoms. It appears simpler to the author to regard the complex as a whole rather than the individual atoms as carriers of the electron. Adopting these ideas, the annexed formula is proposed for the

pyrylium salts, which represents the negative group as freely mobile in the "second" zone and attached to no particular atom, but to the total complex. The fourth carbon valencies are disposed in such a manner as to indicate that one of them resembles the carbon atom of triphenylmethyl, and to express the possibility of the return of the hydroxyl group in the formation of pseudo-bases to either the  $\alpha$ - or the  $\gamma$ -carbon atom. When this has occurred, the remaining valencies arrange themselves to ordinary double bonds; it is also shown that the  $\beta$ -carbon atoms cannot combine with the hydroxyl. Since this conception can readily be expanded to triphenylmethyl and to the nitrogen atoms of azines, oxazines, and thiazines, a uniform conception of a large class of dye-salts is secured.

H. W.



**Syntheses of Methylenecoumarins.** L. CLAISEN (*Ber.*, 1920, **53**, [B], 322—325).—In a recent communication (A., 1919, i, 340), Adams and Rindfuss have described the action of bromine on acetylated *o*-allylphenols and the elimination of the bromine from the product by boiling alcoholic potassium hydroxide, whereby they obtain substances which they consider to be methylenecoumarans of the type  $C_6H_4 \langle \overset{CH_2}{O} \rangle C:CH_2$ . The author points out that he has used this process previously (A., 1913, i, 1175; 1919, i, 266), and that it yields coumarones of the type  $C_6H_4 \langle \overset{CH}{O} \rangle CMe$ . Whilst agreeing with Adams and Rindfuss that the compound  $C_6H_4 \langle \overset{CH_2}{O} \rangle CH \cdot CH_2Br$  is formed as an intermediate stage, he does not consider that the further elimination of hydrogen bromide must of necessity cause the final production of a substance with the double bond in the side-chain, since, under the experimental conditions, one of the two bonds would almost certainly pass to the nucleus. Further, the observation of Adams and Rindfuss that their "methylenecoumaran" yields a monobromo-derivative from which bromine cannot be removed by alcoholic potassium hydroxide or silver nitrate, is most readily explained on the assumption that it is a methylcoumaran brominated in the nucleus.

H. W.

**4'-Methoxy-1'-naphthyl-2-chromone.** S. RUHEMANN and S. I. LEVY (*Ber.*, 1920, **53**, [B], 265—274).—4-Methoxy-1-naphth-aldehyde, b. p. 200—202°/10 mm., is converted by ethyl acetate and metallic sodium into *ethyl β-4-methoxy-1-naphthylacrylate*,  $OMe \cdot C_{10}H_6 \cdot CH:CH \cdot CO_2Et$ , yellow prisms, m. p. 59°, which is readily hydrolysed to the corresponding acid, m. p. 215° (compare Rousset, A., 1899, i, 296; Windaus and Bernthsen-Buchner, A., 1917, i, 670). The latter is reduced by sodium amalgam to *β-4-methoxynaphthylpropionic acid*, colourless needles, m. p. 163—164° (Windaus and Bernthsen-Buchner, *loc. cit.*, give 165—166°), the *silver salt* and *ethyl ester*, colourless oil, b. p. 206—207°/10 mm., of which are described. Attempts to convert the acid into a hydrindone by means of phosphorus pentachloride and aluminium chloride were unsuccessful, the product being an oil, which did not crystallise and could not be distilled without decomposition.

*Ethyl αβ-dibromo-β-4-methoxy-1-naphthylpropionate*,

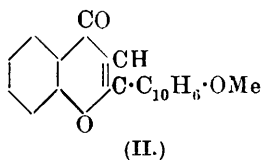
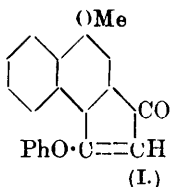
$OMe \cdot C_{10}H_6 \cdot CHBr \cdot CHBr \cdot CO_2Et$ ,

colourless needles, m. p. 108—109° (decomp.), is obtained in quantitative yield from the unsaturated ester and bromine in carbon disulphide solution. It is a somewhat unstable substance, which readily decomposes when gently warmed; it is converted by alcoholic potassium hydroxide solution into *4-methoxy-1-naphthylpropionic acid*, yellow needles, m. p. 159° (decomp.), from which



4-methoxy-1-naphthyl methyl ketone, colourless prisms, m. p. 72—73°, is prepared by prolonged treatment with boiling water. Methoxynaphthylpropionic acid cannot be esterified in the usual manner; thus, treatment with boiling 2—3% alcoholic hydrogen chloride converts it into ethyl  $\beta$ -chloro-4-methoxy-1-naphthylacrylate,  $\text{OMe} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CCl} : \text{CH} \cdot \text{CO}_2\text{Et}$ , yellow, viscous oil, b. p. 230—240°/15 mm. (partial decomp.). Methyl 4-methoxy-1-naphthylpropionate, colourless needles, m. p. 97°, is prepared from the acid, methyl sulphate, and potassium hydroxide, whilst the ethyl ester, yellow prisms, m. p. 81—82°, is similarly obtained, but in very poor yield, with the aid of ethyl iodide.

Ethyl  $\beta$ -phenoxy- $\beta$ -4-methoxy-1-naphthylacrylate is prepared as

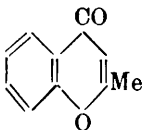


a viscous, red oil, which did not show any tendency to crystallise, and which was not further purified by the action of sodium phenoxide on ethyl  $\beta$ -chloro- $\beta$ -4-methoxy-1-naphthylacrylate; it was hydrolysed by methyl-alcoholic potassium hydroxide to a mixture of the corresponding acid, brown prisms, m. p. 180—181° (decomp.), and the phenyl ether of 3-hydroxy-8-methoxy- $\alpha\beta$ -naphthind-1-one (I), colourless prisms, m. p. 186—187°.

Successive treatment of  $\beta$ -phenoxy- $\beta$ -4-methoxy-1-naphthylacrylic acid with phosphorus pentachloride and aluminium chloride yields 4'-methoxy-1'-naphthyl-2-chromone (II), pale yellow needles, m. p. 177—178°. H. W.

**Formation of Chromones.** S. RUHEMANN (*Ber.*, 1920, **53**, [B], 285—287).—The methods available for the synthesis of chromones (Ruhemann, T., 1900, **77**, 1184; 1901, **79**, 470, 918, 1185; 1902, **81**, 419; Simonis and Rennert, A., 1914, i, 980) suffer under the disadvantage that the yields are very small. The author has therefore endeavoured to synthesise these substances from ethyl  $\beta$ -chlorocrotonate, using a procedure which, in the aromatic series, readily yielded the flavones; although preparation can be effected in this manner, the yields are unsatisfactory.

2-Methylchromone (annexed formula), colourless needles, m. p. 72—73°, is obtained by the successive action of



phosphorus pentachloride and aluminium chloride on  $\beta$ -phenoxycrotonic acid. Similarly,  $\beta$ -p-tolylcrotonic acid, colourless needles, which gradually decompose when heated, softening at 145° and becoming completely molten at about 159—160° (ethyl ester, colourless oil, b. p. 152—153°/14 mm.), is trans-

formed into 2:6-dimethylchromone, colourless prisms, m. p. 103—104°; the latter, like other chromones (Ruhemann, T., 1902,

81, 419), yields a *platinichloride*,  $(C_{11}H_{10}O_2)_2 \cdot H_2PtCl_6$ , orange prisms, which darken when heated and have m. p.  $185^\circ$  (decomp.).  
H. W.

**The Parent Substance of Adrenaline.** KARL W. ROSENMUND and H. DORNSAFT (*Ber.*, 1920, **53**, [B], 317—318. Compare this vol., i, 56).—In reply to the criticism of Knoop (this vol., i, 161), the authors point out (i) that adrenaline is produced in such small quantity in the organism that it is probable that the main processes of degradation of amino-acids are not concerned with its formation, and (ii) that the sequence of changes of amino-acids which they have postulated is not hypothetical, but is based on changes which have been established experimentally for micro-organisms.

H. W.

**The Identity of Aribine with Harman.** ERNST SPÄTH (*Monatsh.*, 1919, **40**, 351—359).—The fact that aribine can be sublimed without decomposition is difficult to reconcile with the molecular weight required by Rieth's formula,  $C_{23}H_{20}N_4$  (*Annalen*, 1861, **120**, 247). A comparison of the alkaloid with harman,  $C_{12}H_{10}N_2$  (Fischer, A., 1901, i, 405), revealed the complete identity of the bases (m. p.  $237$ — $238^\circ$  in a vacuum), of their hydrochlorides (each showing intense blue fluorescence in acid solution), of their aurichlorides (darkening in a vacuum at  $207^\circ$  and melting at  $211$ — $213^\circ$  [decomp.]), of their platinichlorides (straw-yellow needles, which turn brown in a vacuum at  $255$ — $260^\circ$ , and are not melted at  $280^\circ$ ), and of their picrates (yellow crystals, which become brown in a vacuum at  $215^\circ$ , dark brown at  $240^\circ$ , and black at  $250$ — $255^\circ$ ).

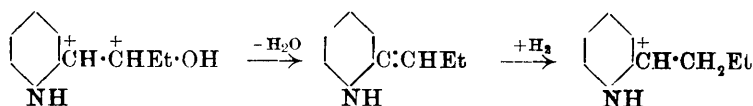
J. K.

**Some New Compounds of Caffeine and Theobromine, Soluble in Water.** J. ABELIN (*Apoth. Zeit.*, **34**, 316; from *Chem. Zentr.*, 1919, iii, 957).—The alkali and alkaline-earth salts of aromatic carboxylic acids and of all  $\omega$ -methylsulphonic acids of carbo- and hetero-cyclic amines yield complex compounds with caffeine and theobromine which are freely soluble in water and, in part, are of therapeutic value. Since aqueous solutions of *o*-acetoxybenzoic acid are readily decomposed, with elimination of acetic acid when slightly warmed, the preparation of *calcium caffeine-o-acetoxybenzoate* is effected by suspending calcium *o*-acetoxybenzoate (100 grams) in anhydrous alcohol or acetone (500 c.c.), and, with continuous stirring, adding a solution of caffeine (55 grams) in chloroform; the solvent is subsequently allowed to evaporate at a low temperature. The purity of the product is tested by treating its aqueous solution with ferric chloride, which should yield a coffee-brown precipitate, but not a violet coloration (absence of salicylic acid). *Calcium theophylline-o-acetoxybenzoate* is similarly prepared from solutions of theophylline in pyridine or benzyl alcohol. The caffeine and theophylline compounds of the  $\omega$ -methyl-

sulphonates of the amines are prepared by mixing solutions of equimolecular quantities of the components in water and evaporating the solutions on the water-bath at a low temperature, or, if the amine salt is insufficiently stable to withstand this treatment, a solution of caffeine in chloroform is added to a suspension of the sodium salts of the  $\omega$ -methylsulphonic acids of *p*-phenetidine (neraltine), of 4-aminoantipyrine (melabrin), of aniline, *p*-toluidine, or naphthylamine in alcohol, acetone, or chloroform, and the solvent is removed with continuous stirring at a gentle temperature.

H. W.

**The Ability of Plants to Form Optical Antipodes.** KURT HESS and WILHELM WELTZIEN (*Ber.*, 1920, 53, [B], 119—129).—The normal products of animal metabolism occur in optically active forms and never in their possible antipodes; an apparent exception to this rule is found in the production of optically inactive lactic acid by the fermentation of dextrose, but in this case it has been established that methylglyoxal is an intermediate product, from which, by an intramolecular Cannizzaro reaction, the lactic acid is finally formed, that is, the final stage is not an enzymic process. In the case of the plant organism, on the other hand, optical antipodes are not infrequently produced simultaneously; examples of this are coniine and methylconiine in *Conium maculatum*, pelletierine, isopelletierine and methylisopelletierine, atropine, laudanine, scopoline, paricine, cryptopine, arabine, cevadine, delphinine, and delphinidine. The production of optically inactive bases which contain at least one asymmetric carbon may be ascribed to one of the following causes: (i) racemisation may have occurred during the treatment of the plant with extracting solvents, (ii) racemisation of a primarily formed optically active alkaloid may have occurred within the plant during its life, and (iii) formation of the alkaloid may be brought about by "symmetrical" processes, either by symmetrical enzymes or by total or partial processes in which enzymes do not play a part. Thus, coniine may possibly be formed in the following manner:



which would be analogous to the production of *dl*-lactic acid from dextrose, with intermediate formation of methylglyoxal. The possibility indicated in (i) may be exemplified by atropine, since *l*-hyoscyamine is readily racemised by dilute alkali at the ordinary temperature and by preservation of its alcoholic solution, whilst protracted treatment with potassium carbonate solution is used in extracting the alkaloid from *Atropa belladonna*. Pelletierine and the allied substances have been shown to be readily racemised, but not under conditions such as are observed in their extraction, whilst,

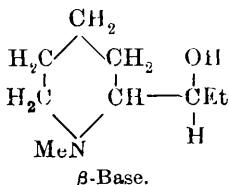
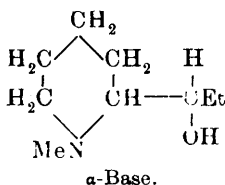
also, no activity is observed in the fresh extracts. *d*-Coniine and *d*-methylconiine are racemised with such difficulty that it is impossible to assume that racemisation occurs in the process of extraction or within the living plant. The case of scopoline is somewhat different, and it appears impossible to attribute the optical inactivity of the natural product to any of the three causes above-mentioned, since King (T., 1919, **115**, 476, 974) has shown that the active base is by no means readily racemised, and an explanation on the lines of that given for *dl*-lactic acid is out of the question. There would thus appear to be an example of a fundamentally different mode of action in the animal and the plant organism.

[In part with (FRL.) H. KAULLA.]—Coniine is not racemised when heated with concentrated hydrochloric acid during 104 hours at about 200° (compare Hess and Eichel, A., 1918, i, 34). Similarly, *d*-methylconiine is unchanged by similar treatment during 120 hours, by the action of ethyl-alcoholic sodium ethoxide solution during 12 hours at 200°, or of aqueous ethyl-alcoholic sodium solution under the same conditions, or by boiling alcoholic potassium hydroxide solution during 45 hours. H. W.

**The Asymmetric, Tervalent Nitrogen Atom. III. Methyl-dihydroisopelletierine and *dl*-Methylconhydrine [Methyl-dihydroconhydrinone].** KURT HESS (*Ber.*, 1920, **53**, [B], 129—139).—In previous communications (A., 1919, i, 345; this vol., i, 86) it has been shown that methylisopelletierine and *dl*-methylconhydrinone are structurally identical, racemic compounds, the isomerism of which can only be explained by the assumption of a second asymmetric centre in addition to the asymmetric carbon atom, which can only be the tervalent nitrogen atom. Since each compound is oxidised to piperidine-2-carboxylic acid and reduced to *dl*-methylconiine, it appeared that the stereoisomerism was in some manner conditioned by the presence of the carbonyl group. It is now found, however, that the four amino-alcohols obtained by reduction of methylisopelletierine and *dl*-methylconhydrinone are all different, so that the isomerism of the parent substances persists in the corresponding alcohols. The carbonyl group of the ketones cannot therefore have the importance which was previously attributed to it, and the cause of the isomerism is to be sought in the arrangement of the groups around the nitrogen atom. If, however, the oxygen atom is entirely removed, the isomerism disappears. It may be further noted that the methiodides of the hydramines of both series are different, and afford a rather unusual example of asymmetric arrangement in a compound of the type N(AABC)X; a similar instance has been observed by Freund and Kessler (A., 1919, i, 283) in the quinoline series.

Methylisopelletierine is readily reduced by sodium amalgam and water at the ordinary temperature to a mixture of *α*-methyl-dihydroisopelletierine, b. p. 101—106°/15 mm., and slightly impure

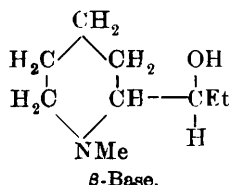
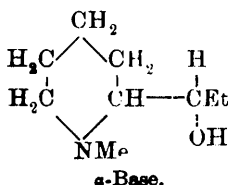
*β*-methyldihydroisopelletierine, b. p. 115—120°/15 mm. (annexed formulæ), which are separated by fractional distillation.



The α-base does not yield crystalline salts with the halogen acids or with chloroplatinic acid, but gives a crystalline methiodide.

m. p. 176°, an oily *picrate*, and an oily *m*-nitrobenzoyl derivative, b. p. ca. 220°/17 mm. The β-base gives a *methiodide*, cubes, m. p. 176—177°, a *picrate*, prisms, m. p. 123—124°, and an oily *m*-nitrobenzoyl derivative, which could not be distilled without almost complete decomposition. Reduction of either base by phosphorus and hydriodic acid at 125—135° gave *dl*-methylconiine, identified as the platinichloride and aurichloride.

α-*dl*-Methylconhydrine, b. p. 97—99°/16 mm., and β-*dl*-methylconhydrine, b. p. 91—101°/15 mm. (annexed formulæ), are obtained by the action of formaldehyde and formic acid on the corresponding hydramines.



The α-base gives a *methiodide*, prisms, m. p. 178—179°, a *picrate* (+0.5EtOH), rods,

m. p. 79—80°, and an oily *m*-nitrobenzoyl derivative. The *methiodide* of the β-base crystallises in prisms, m. p. 174°, the *picrate* forms irregular plates and cubes, m. p. 133—134°, and the *m*-nitrobenzoyl derivative is an oil. Reduction of either base by hydriodic acid and red phosphorus yields *dl*-methylconiine.

Isomerism of the amino-alcohols is not so sharply marked as that of the ketones, since in the former case the m. p.'s of the salts are nearly identical, whilst in the latter case they differ by 30—40°; the individuality of the salt is, however, readily demonstrated by the mixed melting-point method.

H. W.

**The Asymmetric, Tervalent Nitrogen Atom. IV. Non-existence of Ladenburg's *iso*Coniine.** KURT HESS and WILHELM WELTZIEN (*Ber.*, 1920, **53**, [B], 139—149).—Some years ago Ladenburg (*A.*, 1906, i, 692, and previous abstracts) described the preparation of *isoconiine*, and explained its isomerism with coniine by the hypothesis of an asymmetric, trivalent nitrogen atom. On theoretical grounds, the authors have been led to doubt the existence of this instance, since the salts of coniine and *isoconiine* have identical melting points, which is unusual in a case of this kind, whilst, secondly, *dl*-methylconiine (preceding abstract) is incapable

of existence in the corresponding isomeric forms, and the same is therefore probably true for coniine itself, and, thirdly, *l*-coniine has been synthesised by Löffler (A., 1909, i, 180) and found to be identical with the natural substance. They have therefore repeated Ladenburg's work, and obtained results which are practically identical with his. The possibility that *isoconiine* as prepared in this manner is contaminated with an impurity which affects the specific rotation, but is eliminated in the purification of the salts, has been examined by adopting a different mode of synthesis, which is found to yield a material identical in all respects with natural *d*-coniine. The higher optical activity of Ladenburg's synthetic coniine preparation is therefore to be attributed to the presence of impurities, and *isoconiine* is to be deleted from the literature.

Ladenburg's synthesis has been slightly modified. Methyl- $\alpha$ -picolylalkine is reduced by phosphorus and hydriodic acid, but as the product is found to contain about 65% of 2-allylpyridine, the conversion to the propyl derivative is completed by means of hydrogen in the presence of platinum. The *dl*-coniine is prepared by reduction of 2-propylpyridine by sodium and alcohol, and is resolved by *d*-tartaric acid. The hydrogen tartrate and platinum-chlorides of the synthetic and natural bases appeared identical in all respects, but the synthetic base had  $[\alpha]_D + 19.01^\circ$ , whereas the natural product had only  $[\alpha]_D + 15.21^\circ$ .

The preparation of *dl*-coniine from methyl  $\alpha$ -picolylalkine has been effected in a somewhat different manner, in that the substance is first converted into the piperidine derivative by hydrogen in the presence of platinum, and the hydroxy-group is subsequently reduced by treatment with phosphorus and hydriodic acid, followed by zinc and sulphuric acid; in this manner, the formation of an allyl derivative is avoided. The racemic base is resolved by *d*-tartaric acid; the specific rotation of the hydrogen tartrate is  $+20.06^\circ$  in alcoholic solution, whilst the base obtained from it has  $[\alpha]_D^{17} + 14.96^\circ$ , which agrees well with the specific rotation of the natural product.

H. W.

**A Radicle with Quadrivalent Nitrogen.** BRUNO EMMERT (*Ber.*, 1920, 53, [B], 370—377).—Dimethyl- or diethyl-tetrahydrodipyridyl,  $R \cdot N \begin{smallmatrix} \text{CH:CH} \\ \text{CH:CH} \end{smallmatrix} \text{CH} \cdot \text{CH} \begin{smallmatrix} \text{CH:CH} \\ \text{CH:CH} \end{smallmatrix} N \cdot R$  (Hofmann, A., 1881, 921; Emmert, A., 1909, i, 602; 1917, i, 221; 1919, i, 455), is soluble in alcohol, yielding a yellowish-brown solution, which, slowly at the ordinary temperature, but more rapidly when warmed, becomes deep blue; the blue coloration disappears immediately when the solution is shaken with air, but slowly reappears, and can be again removed until a molecule of oxygen has been absorbed for each molecule of substance. The phenomena are thus analogous with those observed by Schmidlin (A., 1908, i, 623) in the case of triphenylmethyl. In the present instance, there is the possibility

of the formation of two radicles (annexed formulæ, I and II) containing, respectively, a quadrivalent nitrogen or a tervalent carbon atom, which on oxidation should yield a pyridinium hydroxide or a peroxide; actually, the formation of methylpyridinium hydroxide from dimethyltetrahydrodipyridyl (identified as the chloride and platinichloride) is established. In the case of benzyltetrahydrodipyridyl, the blue coloration of the alcoholic solution is only developed on warming. Solutions in ether are yellow, and do not become blue. Solutions in chloroform are intermediate in their properties between those in ether and alcohol; the yellow solution, when preserved with exclusion of air, slowly becomes pale green to bluish-green, which may be regarded as a mixture of the yellow and blue colorations. The following experiments show that the blue solutions actually contain the radicle (I); the alcoholic solutions are instantaneously decolorised by iodine and yield *N*-alkylpyridinium iodides, as is shown by the isolation of these substances and by the estimation of ionisable iodine in the crude products. Addition of iodine to the yellow, ethereal solutions causes partial resinification; allylpyridinium iodides are also formed in small amount, together with larger quantities of yellow, amorphous powders, which could not be further purified, but which are shown to contain an atom of iodine for each pyridine nucleus. A mixture of alkylpyridinium iodide and the yellow, amorphous iodo-compound is formed from the chloroform solution.

In the case of triphenylmethyl, the degree of dissociation, and consequently the intensity of colour of the solution, diminishes with decreasing temperature. The blue, alcoholic solutions of the dialkyltetrahydrodipyridyls become violet-red at  $-80^{\circ}$ , whilst that of the dibenzyl derivative changes to brown, the colour in each case being restored when the solution is warmed; the reason of the non-disappearance of the colour has not been elucidated.

The tendency of the dialkyltetrahydrodipyridyls to dissociate into radicles is ascribed to the weakening of the valency uniting the  $\gamma$ -carbon atoms by the demands of the numerous double bonds, and cannot be ascribed to steric hindrance, which has been so frequently advanced as a theory in the triphenylmethyl series. H. W.

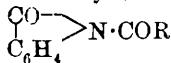
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### The Action of Ethyl Chloroformate on Pyridine and Quinoline. THOMAS HOPKINS (T., 1920, 117, 278—282).

**Crystallographic Properties of a Compound  $C_{11}H_9O_2N$ .** A. JOHNSEN (*Centr. Min.*, 1919, 33—34).—The compound, which possibly has the structure  $CHPh:C \begin{matrix} \diagup CO \\ \diagdown CO \\ NH \cdot CH_2 \end{matrix}$ , melts at  $138.5 \pm 0.5^{\circ}$  (decomp.), and crystallises from benzene in short columns with indistinct end faces;  $a:b:c = 1.335:1.057;$

$\beta = 114^\circ 18\frac{1}{2}'$ .  $D^{16}_D$  1.345. Cleavages were observed parallel to the faces {100} and {101}. The optic axial angle is large, and  $n_D$  1.756. E. H. R.

**Constitution of Acylantranilic Anhydrides.** G. SCHROETER (*Ber.*, 1920, **53**, [B], 230—232).—In a recent communication (this vol., i, 181), Heller and Lauth have described the preparation of hydrazino-derivatives of simple and complex acylantranilys, to which they have attributed the general structure



instead of  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{N} = \text{C} \cdot \text{R} \end{array}$ . The author, however, regards the form-

ation of the hydrazine additive products as additional evidence in favour of the lactonic formulæ; he points out, for example, that the anhydride of formylantranilic acid may be regarded as isocoumarin, in which a CH

group is replaced by nitrogen, and that, therefore, their hydrazino-compounds may be similarly formulated (annexed formulæ, I and II). The lactone formula further explains why acylantranilic

acids which contain the group  $\cdot\text{NH} \cdot \text{CO} \cdot$  readily form unimolecular anhydrides, owing to preliminary change into the desmotropic form  $\cdot\text{N} : \text{C}(\text{OH}) \cdot$ , whereas those in which this desmotropic change is structurally impossible give bimolecular anhydrides. H. W.

### Products of the Action of Oxalyl Chloride on Acid Anilides.

R. STOLLÉ and M. LUTHER (*Ber.*, 1920, **53**, [B], 314—317).—When acetanilide is heated with rather more than a molecular proportion of oxalyl chloride in carbon disulphide solution, it yields a compound,  $\text{C}_{10}\text{H}_7\text{O}_3\text{N}$ , m. p.  $143^\circ$  (not quite definite), which, mainly by reason of the readiness with which it is decomposed by water into acetic and oxanilic acids, is regarded as 4:5-diketo-3-phenyl-2-methylenetetrahydro-oxazole,  $\text{O} \begin{array}{c} \text{C}(\text{CH}_3) \\ \diagup \quad \diagdown \\ \text{CO} - \text{CO} \end{array} \text{NPh}$ . When warmed with alcohol, it gives 4:5-diketo-2-ethoxy-3-phenyl-2-methyltetrahydro-oxazole, colourless needles, m. p.  $98^\circ$ . Under similar conditions, diethylacetanilide and oxalyl chloride (1:1) give 4:5-diketo-3-phenyl-2-diethylmethylenetetrahydro-oxazole, m. p.  $69^\circ$ .

The compounds obtained by Figée (*A.*, 1915, i, 869) from molar quantities of oxalyl chloride and propionanilide or phenylacetanilide are to be regarded as 4:5-diketo-3-phenyl-2-ethylidenetetrahydro-oxazole and 4:5-diketo-3-phenyl-2-benzylidenetetrahydro-oxazole. H. W.

**Preparation of Octanitrodiphenylethylenediamine.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 300082; from *Chem. Zentr.*, 1920, ii, 188).—Octanitrodiphenylethylenediamine,



$C_6H_2(NO_2)_3 \cdot N(NO_2) \cdot CH_2 \cdot CH_2 \cdot N(NO_2) \cdot C_6H_2(NO_2)_3$ , is prepared by the action of concentrated nitric acid on 2:4:2':4'-tetranitrodiphenylethylenediamine or 2:4:6:2':4':6'-hexanitrodiphenylethylenediamine; it crystallises from concentrated nitric acid in colourless, rhombic prisms, m. p. 213° (violent decomp.), and is almost insoluble in the usual organic media. It is an extremely sensitive explosive.

H. W.

**Absorptive Power of Uric Acid towards Dyes.** ALBE BENOIT (*Compt. rend. soc. biol.*, 1919, **82**, 1051—1052; from *Chem. Zentr.*, 1920, i. 168).—Uric acid has the power of adsorbing precipitated colloids from their solutions. If methylene-blue is administered to a subject who separates uric acid freely, the sediment is coloured blue. If a trace of dye is added to a hot saturated solution of uric acid, coloured crystals of the latter are deposited from the cold solution. When a cold saturated solution of a normal urate is treated with a small quantity of a soluble dye and then acidified with a trace of hydrochloric acid, the precipitated uric acid adsorbs the dye, and can even cause complete decolorisation of the solution.

H. W.

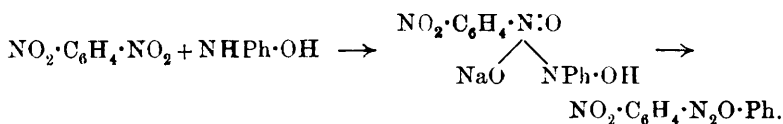
**State of Uric Acid in Solution.** ALBE BENOIT (*Compt. rend. soc. biol.*, 1919, **82**, 1052—1053; from *Chem. Zentr.*, 1920, i. 168).—Uric acid may be present in solution in two physically different conditions, in one of which it is stable, flocculent, and crystalline, and cannot adsorb dyes, whilst in the other it is metastable; it is found in the latter condition in supersaturated solution in urine. Uric acid is therefore probably more soluble in colloidal solutions than in the corresponding quantity of distilled water at the same temperature.

H. W.

**Action of *N*-Phenylhydroxylamine on Aromatic Nitro-compounds.** JAKOB MEISENHEIMER (*Ber.*, 1920, **53** [B], 358—369).—The action of hydroxylamine on *m*-di- and tri-nitro-compounds leads to the substitution of hydrogen atoms attached to the nucleus by amino-groups, whereas with *o*- and *p*-dinitroaryls, reduction to the corresponding dihydro-derivatives occurs (Meisenheimer and Patzig, A., 1906, i, 642, 652). It is now shown that the reaction with phenylhydroxylamine follows a similar course in each case.

[With IVAN SMOLNIKOV.]—When *m*-dinitrobenzene and phenylhydroxylamine react in methyl-alcoholic solution in the presence of potassium hydroxide, a mixture of azoxybenzene,  $\alpha$ -3-nitro-1-azoxybenzene, yellow needles, m. p. 120—121°, and  $\beta$ -3-nitro-1-azoxybenzene, pale yellow needles, m. p. 86—88°, is obtained. The latter substances are reduced by ammonium sulphide to 3-nitro-1-hydrazobenzene, yellow crystals, m. p. 84—85°, which is oxidised by mercuric oxide to 3-nitro-1-azobenzene, m. p. 95—96° (compare

Bamberger and Hübner, A., 1904, i, 117). The course of the condensation is indicated by the scheme:



A similar mixture of azoxy-compounds is obtained from 1:3:5-trinitrobenzene, but in this instance only the more sparingly soluble 3:5-dinitro-1-azoxybenzene, practically colourless crystals, m. p. 170—171°, was isolated.

2:4-Dinitrotoluene yields with azoxybenzene. *α*-benzeneazoxy-2-nitro-*p*-toluene, yellow crystals, m. p. 123—124°, *β*-benzeneazoxy-2-nitro-*p*-toluene, m. p. 119—120°, and a substance, m. p. 160°, which is very probably 2:2'-dinitro-4:4'-azoxytoluene. Reduction of the benzeneazoxynitrotoluene yields the corresponding *hydrazobenzene*, which, without being isolated, was oxidised to *benzeneazo-2-nitro-*p*-toluene*, orange-red needles, m. p. 103—104°, the constitution of which is established by its synthesis from nitrosobenzene and 3-nitro-*p*-toluidine.

The nitro-group appears capable of adding hydroxylamine in the manner described above only if both the ortho-positions with respect to it are free. Thus 2:6-dinitrotoluene is converted into 2:2'-dinitro-6:6'-azoxytoluene, nearly colourless crystals, m. p. 189—190° (Brand and Zoller, A., 1907, i, 755).

The additive power of nitro-groups in the *m*-, di- and tri-nitro-compounds is greatly influenced by the presence of other substituents; preliminary experiments show that 2:4:6-trinitrotoluene and 2:4:6-trinitrophenetole react in a quite different manner (which has not been further examined), whilst 2:4:6-trinitro-*m*-xylene remains unaffected.

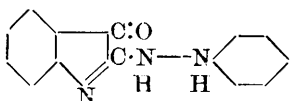
When 1:3:5-trinitrobenzene and phenylhydroxylamine are dissolved in alcohol, a crystalline *substance* is slowly deposited (pale yellow leaflets or needles, m. p. 123—124°), which is formed from 1:3:5-trinitrobenzene (2 molecules) and azoxybenzene (1 molecule), the latter being obviously formed by the auto-decomposition of phenylhydroxylamine. *m*-Dinitrobenzene behaves similarly, yielding *m*-dinitrobenzeneazoxybenzene,  $\text{C}_{18}\text{H}_{14}\text{O}_5\text{N}_4$ , yellow plates, m. p. 52—54°. Azoxybenzene was also found to give additive *products* with 1:3:5-trinitrobenzene, with 2:4:6-trinitrotoluene (yellow leaflets, m. p. 64—66°), and with *m*-dinitrobenzene, but not with 2:4:6-trinitrophenetole or 2:4-dinitrotoluene. Azobenzene was less reactive, but yielded an additive compound with trinitrobenzene (compare Hofmann and Kirmreuther, A., 1910, i, 548), but not with 2:4:6-trinitrotoluene, 2:4:6-trinitrophenetole, *m*-dinitrobenzene, or 2:4-dinitrotoluene.

H. W.

**Azo-derivatives of Indoxyl.** J. MARTINET and O. DORNIER (*Compt. rend.*, 1920, **170**, 592—594).—Azo-derivatives of indoxyl

may readily be prepared by adding to a mixture of ice and indoxyl neutralised with sulphuric acid, the requisite amount of a diazo-compound. In this way the authors have prepared: *o*-Tolueneazoindoxyl, m. p. 249° (decomp.). *m*-Tolueneazoindoxyl, m. p. 232° (decomp.). *p*-Tolueneazoindoxyl, m. p. 256° (decomp.). *m*-4-Xyleneazoindoxyl, m. p. 244° (decomp.).  $\psi$ -Cumeneazoindoxyl, m. p. 245° (decomp.).  $\alpha$ -Naphthaleneazoindoxyl, m. p. 202° (decomp.).  $\beta$ -Naphthaleneazoindoxyl, m. p. 220° (decomp.).

All the m. p.'s given are approximate owing to decomposition.



Benzeneazoindoxyl, when reduced in alkaline solution by sodium hyposulphite, gives aniline, ammonia, and indirubin.

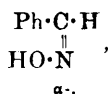
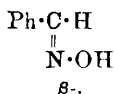
The authors discuss the structure of these azo-compounds, and suggest as a possible constitution the formula annexed as an alternative to that supported by Baeyer (compare A., 1884, 74) and Heumann (compare *Ber.*, 1893, 26, 226) or the one supported by Heller (compare A., 1907, i, 442).

W. G.

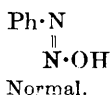
### Diazo-compounds. Thermochemical Investigations.

W. SWIENTOSLAWSKI (*Ann. Soc. d'Encour. Sci. Expt.*, 1917, Suppl. No. 7. Reprint 15 pp.).—In part a very brief résumé of work already published (compare A., 1909, ii, 547, 864; 1910, ii, 588, 691; 1911, ii, 188, 967; 1914, ii, 105, 107; 1918, ii, 32).

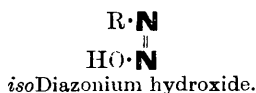
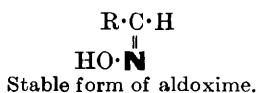
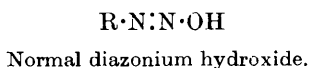
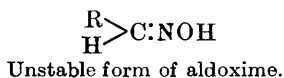
The author has measured the heat of reaction of varying proportions of sodium hydroxide on different oximes and of excess of hydrochloric acid on the same oximes, and on these results bases a discussion of the constitution of the oximes and their relationship to the diazonium hydroxides. The heats of reaction indicate that  $\alpha$ -benzaloxime is more strongly acid than  $\beta$ -benzaloxime, and in this respect closely resembles acetaldoxime. Accordingly, for the two oximes the following structures are suggested:



and from these the structures of the diazo-compounds are deduced as follows, the *iso*-form being more acid than the normal form:



Finally the author puts forward the hypothesis that in certain compounds containing nitrogen the atom (or atoms) undergo a deformation, the three valencies of nitrogen being displaced, and the atom loses one of its planes of symmetry. This deformation is accompanied by an increase of acidity. Thus there is:



the nitrogen atom indicated by **N** having undergone deformation.

In a final chapter the author discusses the relative merits of Cain's and Blomstrand's structural formulæ for diazo-compounds, and quotes certain facts which, in his opinion, are opposed to Cain's formula. At the same time he considers that Blomstrand's formula does not offer an explanation of all the known properties of the diazo-compounds.

W. G.

**Condensation Products from *p*-Aminoazobenzene and Ketones or Aldehydes.** G. REDDELIEN (*Ber.*, 1920, 53, [B], 340—344).—Benzophenone is scarcely affected by being heated with *p*-aminoazobenzene even after addition of hydrobromic acid (compare this vol., i, 315); reaction, however, occurs readily if benzophenoneanil (*A.*, 1913, i, 1203) is substituted for the ketone, the necessary condition consisting in the removal of the liberated aniline, which is readily effected by performing the operation in a vacuum at 180°; the *p*-diphenylmethylenearminoazobenzene,  $\text{CPh}_2 : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{Ph}$ , forms coarse, orange-yellow crystals, or, less frequently, large, less intensely coloured plates, both varieties having m. p. 123°. It yields an orange-red *monohydrochloride* and a dark red *dihydrochloride*, both of which are rapidly decomposed by traces of moisture into aminoazobenzene hydrochloride and benzophenone. *p*-Fluorenylideneaminoazobenzene, long, orange-yellow, strongly dichroic needles, m. p. 141—142°, is prepared similarly.

For comparative purposes, the following condensation products of aldehydes and *p*-aminoazobenzene have been prepared: *p*-cinnamylideneaminoazobenzene,  $\text{CHPh} : \text{CH} : \text{CH} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{Ph}$ , orange-yellow leaflets, m. p. 137—138° (*hydrochloride*, orange-red, crystalline powder); *p*-dimethylaminobenzylideneaminoazobenzene, orange-yellow crystals, m. p. 174—175°; *di-p*-dimethylaminophenylmethylenearminoazobenzene ( $\text{NMe}_2 \cdot \text{C}_6\text{H}_4$ )<sub>2</sub> :  $\text{C} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{Ph}$ , orange-red needles, m. p. 232—233°. The halochromic phenomena on solution in concentrated sulphuric acid are shown in the following table:

	Colour of substance.	Colour of solution.
Benzylideneaminoazobenzene.....	orange-yellow.	orange-red.
Cinnamylideneaminoazobenzene .....	orange-yellow.	purple-red.
Diphenylmethylenearminoazobenzene.	orange-yellow.	orange-red.
Fluorenylideneaminoazobenzene .....	orange.	cinnabar-red.
<i>p</i> - Dimethylaminobenzylideneaminoazobenzene .....	orange-yellow.	orange-yellow.
Di- <i>p</i> -dimethylaminophenylmethylenearminoazobenzene .....	orange.	orange.

It appears, therefore, that the halochromy is noticeably increased when the C:N-group is conjugated with a neighbouring C:C-group, a phenomenon which is also observed with unsaturated anils and ketones. Similarly, the hydrochloride is rendered more stable by the presence of the conjugated C:C-group. The non-appearance of halochromy in the two instances last mentioned is probably attributable to the smaller basicity of the aminoazobenzene residue as compared with the anil residue; as a consequence, salt formation may occur at a dimethylamino-group and therefore not cause halochromy.

H. W.

### **A New Method for Preparing Esters of Amino-acids.**

**Composition of Caseinogen.** FREDERICK WILLIAM FOREMAN (*Biochem. J.*, 1919, **13**, 378—397).—The outlines of the process are as follows: The amino-acids are converted into their dry lead salts, which are suspended in absolute alcohol and converted into the ethyl esters by saturation with dry hydrogen chloride. After removal of the free hydrochloric acid and the alcohol, the ester hydrochlorides are dissolved in dry chloroform, and the free esters liberated by shaking the solution with anhydrous barium hydroxide. The chloroform is removed by evaporation under reduced pressure, and the esters are dissolved in anhydrous ether. Subsequently they are fractionally distilled in the usual manner. This process avoids considerable loss of esters by hydrolysis, which occurs by the use of aqueous solutions in the usual procedure. This method has already yielded results of value, in that some of the deficit in the amino-acid content of caseinogen has been accounted for. The author gives the following details of the percentage composition of caseinogen, partly from the results of his own work and partly from other sources: Glycine, 0.45; alanine, 1.85; valine, 7.93; leucine, 9.7; proline, 7.63; phenylalanine, 3.88; glutamic acid, 21.77; aspartic acid, 1.77; new syrups, 14.34; lysine, 7.62; histidine, 2.5; arginine, 3.81; tryptophan, 1.5; serine, 0.5; tyrosine, 4.5; hydroxyproline, 0.23; diaminotrihydroxydodecanic acid, 0.75; ammonia, 1.61; sulphur, 0.76; phosphorus, 0.85; substances of peptide nature obtained on hydrolysis, 3.41; total, 97.36%.

J. C. D.

**Dissociation of Oxyhæmocyanins.** CH. DHÉRE and A. SCHNEIDER (*Compt. rend. soc. biol.*, 1919, **82**, 1038—1040; from *Chem. Zentr.*, 1920, i, 176—177).—Careful experiments with solutions of pure crystalline oxyhæmocyanin, in some cases in the presence of an antiseptic, show that the substances obtained from the snail and the lobster are readily reducible by physical dissociation.

H. W.

**A Compound of the Hæmocyanin of the Snail with Nitric Oxide.** CH. DHÉRE and A. SCHNEIDER (*Compt. rend. soc. biol.*, 1919, **82**, 1041—1043; from *Chem. Zentr.*, 1920, i, 177).—A solution of the hæmocyanin forms with nitric oxide a crystalline, green dye, which is designated "hæmocyanin nitric oxide."

H. W.

**Liquefaction of Gelatin by Salts.** T. R. BRIGGS and EVELYN M. C. HIEBER (*J. Physical Chem.*, 1920, **24**, 74—75).—Solutions of 5% gelatin were mixed with 33% solutions of zinc chloride, potassium chloride, ammonium nitrate, potassium thiocyanate and magnesium chloride, and with saturated solutions of potassium nitrate and ammonium chloride respectively, and placed in a thermostat at 19°. After thirty minutes the mixture containing potassium chloride had set to a jelly, in twenty-four hours those containing magnesium chloride and ammonium chloride had set, and after thirty-six hours the remainder were still liquid. After dialysis for twenty-four hours the whole of the solutions had set, and on again mixing with zinc chloride, ammonium nitrate, and potassium thiocyanate respectively the jellies liquefied within an hour. It is thus proved that the processes of liquefaction and gelatinisation produced by salts are strictly reversible. J. F. S.

**Presence of Invertase in the Pure Honey of Bees.** ALIN CAILLAS (*Compt. rend.*, 1920, **170**, 589—592).—By the general method of preparation of enzymes by precipitation with alcohol, invertase was isolated in the form of its aqueous solution from a sample of honey. The honey contained approximately 0.05% of the enzyme, which gave all the tests for invertase, including the hydrolysis of sucrose. W. G.

**A Method of Testing the Amylolytic Action of the Diastase of *Aspergillus Oryzæ*.** SELMAN A. WAKSMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 293—299).—The Lintner method for measuring the saccharogenic action of different enzymes on starch should not be used for comparative studies with different enzymes, since the end-products are not the same in the various cases. The starch liquefying (iodine) methods, with the exception of that of Wohlgemuth, do not give the "liquefaction" of starch by enzymes, but measure the reduction of the starch to substances giving no longer any reaction with iodine, which is arbitrary. In the study of the action of enzymes on the starches present or embodied in textiles (process of de-sizing), the Lintner method and its various modifications are unsuitable, since the problem consists in the elimination of starch, and not in the production of sugar. A convenient method for measuring the starch-liquefying power (amylolytic action) of enzymes consists in adding the requisite amount of the latter to 10 c.c. of a 2% paste of raw potato starch, which is maintained at 40°, and observation of the time required for the liquid to become clear; the determination of the end-point may be facilitated by staining the starch, preferably with neutral red. When the stage of hydrolysis corresponding with this end-point is tested with iodine, it is found to be identical with that at which no heavy blue colour is obtained, but only a deep brown to faintly violet-brown colour or faint bluish-violet colour, showing that all the starch paste has been transformed into dextrins.

Comparing the starch-liquefying powers of malt enzymes and

enzymes obtained from *Aspergillus oryzae* (water extract used known commercially as polyzyme), the first are found to give a higher Lintner value, whilst the second give a higher liquefying value. The ratio of the latter to the former in the case of malt preparations is 1:4 to 1:5, whilst in the case of *Aspergillus oryzae* enzyme it is 1:1 to 1:5:1, so that the liquefying power of the latter in comparison to its saccharogenic power is four to six times as great as that of the malt preparations. H. W.

**Consecutive Action of Two Types of Emulsins on Amygdalin.** J. GATAJ (*Compt. rend. soc. biol.*, 1919, 82, 1196—1198; from *Chem. Zentr.*, 1920, i, 299. Compare A., 1914, i, 1099).—If the action of emulsin of almonds on amygdalin is stopped by heating at a period when a portion of the latter remains unattacked, the action can be completed by the subsequent addition of the digestive juice of *Helix pomatia*; the same amounts of hydrocyanic acid and dextrose are formed as when complete decomposition is effected by one ferment only. If the order of addition is reversed, that is, if the emulsin of almonds is added to the amygdalin solution which has been partly decomposed by *Helix* juice and then heated, complete decomposition does not occur, although a certain amount of hydrocyanic acid and of dextrose is formed. Intermediate products are formed under the influence of *Helix* juice which are not further attacked by emulsin of almonds. H. W.

**Bivalent Tin as Chromophore in Aromatic Stannous Compounds and the Preparation of Hexa-aryldistannanes.** ERICH KRAUSE and REINHARD BECKER (*Ber.*, 1920, 53, [B], 173—190).—Alkyl compounds of bivalent tin have been described previously, but their isolation in the pure state has proved impossible. The authors have therefore turned their attention to the corresponding di-aryl compounds, which are found to be stable, crystalline substances. Their most remarkable properties are their intense colour, which must be attributed to the unsaturated tin atom behaving as a chromophore, and their peculiar transformation into hexa-aryl distannanes analogous to the hexa-alkyl compounds described by Grüttner (*A.*, 1918, i, 159).

*Tin diphenyl* is prepared by the addition of finely-powdered stannous chloride to an ethereal solution of a considerable excess of magnesium phenyl bromide; it forms a bright yellow, voluminous, amorphous powder, which has m. p. 130° (to a dark red, viscous liquid), after softening at 126°. Dilute solutions of the substance in benzene are intense yellow to reddish-yellow, and become cloudy and gradually decolorised on exposure to air. The benzene solution becomes dark red, and gives a yellow precipitate on exposure to sunlight. Dry tin diphenyl is rapidly decolorised on exposure to light and air, but it may be preserved unchanged for months in an atmosphere of nitrogen. The freshly prepared material appears to have a normal molecular weight in benzene

solution, but polymerisation soon begins, so that, after a few days, the molecular weight has increased fivefold. In chloroform solution tin diphenyl rapidly absorbs the calculated quantity of bromine and yields tin diphenyl dibromide, which, for purposes of identification, was converted by potassium fluoride into the more readily purified *tin diphenyl difluoride*, colourless, four-sided rods, m. p. above  $360^{\circ}$ .

*Hexaphenyldistannane* is prepared by the treatment of stannous chloride with a large excess of magnesium phenyl bromide at  $100^{\circ}$ , by the action of sodium on tin triphenyl chloride, or by reduction of the latter with sodium and alcohol; it crystallises in colourless, rectangular plates, m. p.  $237^{\circ}$  (corr.) (from benzene in colourless, shining rhombohedra +  $1.5C_6H_6$ ), and is completely stable towards air. It has a normal molecular weight in benzene solution. It immediately reduces silver solutions to metallic silver, even at  $-75^{\circ}$ . It is converted by bromine in chloroform solution at  $-30^{\circ}$  into tin triphenyl bromide.

*Tin di-p-tolyl* is an orange-yellow, amorphous powder, m. p.  $111.5^{\circ}$ , after softening at  $109^{\circ}$ . It is less readily oxidised by air than is tin diphenyl, which, however, it closely resembles in undergoing polymerisation when preserved. Possibly by reason of steric hindrance, tin di-*p*-tolyl, unlike the phenyl derivatives, is not converted into hexa-*p*-tolyl-distannane when heated with an excess of magnesium phenyl bromide at  $100^{\circ}$ ; at a higher temperature a complicated decomposition occurs, tin tetra-*p*-tolyl being formed together with many other substances.

Tin tetra-*p*-tolyl (compare Pfeiffer, A., 1910, i, 724) is converted into the monobromide in pyridine solution, and this is transformed into the hydroxide; the latter is purified and transformed by the requisite halogen acid into *tin tri-p-tolyl chloride*, coarse, rhombic plates, m. p.  $97.5^{\circ}$ , *tin tri-p-tolyl bromide*, colourless rhombohedra, m. p.  $98.5^{\circ}$ , and *tin tri-p-tolyl iodide*, colourless, rhombic plates, m. p.  $120.5^{\circ}$ . *Tin tri-p-tolyl fluoride*, slender, interwoven needles, m. p.  $305^{\circ}$ , and *tin triphenyl fluoride*, colourless, minute prisms, m. p.  $357^{\circ}$ , after darkening at  $345^{\circ}$ , are also described. The latter substance is of interest, since it is so sparingly soluble in cold alcohol, ether, or water that the chloride can be used for the quantitative precipitation of fluorides. *Hexa-p-tolyl-distannane*, colourless, rhombic platelets, m. p.  $145^{\circ}$  (corr.), is prepared by the reduction of tin tri-*p*-tolyl bromide with sodium and alcohol.

*Tin tetra-m-tolyl* forms colourless needles, m. p.  $128.5^{\circ}$ .

The following *o*-tolyl derivatives were prepared from the product obtained by the action of stannic chloride on the quantity of magnesium *o*-tolyl bromide calculated for the formation of tin tetra-*o*-tolyl (instead of a considerable excess, as recommended by Krause and Schmitz, this vol., i, 198); the crude material was purified by conversion into the hydroxide, which was subsequently converted into *tin tri-o-tolyl chloride*, colourless, pointed prisms, m. p.  $99.5^{\circ}$ , *tin tri-o-tolyl bromide*, compact, rhombic plates, m. p.  $99.5^{\circ}$ , and *tin tri-o-tolyl iodide*, hard, rhombic crystals, m. p.  $119.5^{\circ}$ .



*Tin di-p-xylyl*, m. p.  $157^{\circ}$ , after softening at  $155^{\circ}$ , closely resembles the corresponding di-*p*-tolyl compound, but is considerably more stable towards air, so that it may be preserved exposed to air for some considerable time without undergoing change. The following *p*-xylyl derivatives are obtained in the usual manner: *tin tetra-p-xylyl*, colourless, microscopic, four-sided rods or cubes, m. p.  $278^{\circ}$  (corr.); *tin tri-p-xylyl chloride*, colourless, compact crystals, m. p.  $141.5^{\circ}$  (corr.); *tin tri-p-xylyl bromide*, large, six-sided crystals, m. p.  $151^{\circ}$  (corr.); *tin tri-p-xylyl iodide*, large, six-sided plates, m. p.  $159.5^{\circ}$  (corr.); *tin tri-p-xylyl fluoride*, slender, microscopic needles, m. p.  $247^{\circ}$  (corr.); *hexa-p-xylyldistannane* (from tin tri-*p*-xylyl bromide and sodium), colourless, rhombic plates, m. p.  $196^{\circ}$  (corr.).

*Tin tetra-m-xylyl* forms long, rhombic needles, m. p.  $224^{\circ}$  (corr.); it is isolated with greater difficulty than are its isomerides owing to its greater solubility. The tin tri-*m*-xylyl haloids do not crystallise with the exception of the *fluoride*, slender, interwoven needles, m. p.  $209^{\circ}$  (corr.).

*Tin di-a-naphthyl* resembles the corresponding xylyl compound in preparation and properties, but is even less sensitive to air; it has m. p.  $200^{\circ}$  after softening at  $196^{\circ}$ .

H. W.

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### Physiological Chemistry.

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**The Action of Certain Precipitates on the Solution of Red Globules.** ARTHUR VERNES and ROGER DOURIS (*Compt. rend.*, 1920, **170**, 528—529).—The property, which the serum of pig's blood possesses, of dissolving the red globules from sheep's blood, can be destroyed by dissolving in the serum a precipitate formed from ferric thiocyanate and human serum. W. G.

**The Physiological Action of Calcium.** R. HÖBER (*Pflüger's Archiv*, 1917, **166**, 531—608; from *Physiol. Abstr.*, 1917, **2**, 523).—The effect of Ca (ions) in diminishing hæmolysis by narcotics is shared by the ions Sr, Ba, and Mg. Mn and Co are more efficacious than the above, and Ni more efficacious than any of the others. When, however, hæmolysis is produced by hypotonic solutions of sodium chloride, Ca is the most and Ni the least efficacious. When hæmolysis is produced by saponin, the relative inhibitory effect of the ions in question differs with the blood of different animals. In preventing (or diminishing) the toxic action of potassium on skeletal muscle, the ions work in the following order: Ca>Sr>

Mg>Co>Ba>Mn>Ni>Zn, that is, their value corresponds with that in diminishing hæmolysis by hypotonic solutions. In preventing (or diminishing) the toxic action of narcotics on muscle, the ion series reads: Ni>Co, Mn, Ba>Sr, Ca. Further, in preventing (or diminishing) the fibrillar contractions evoked by solutions of sodium chloride, the series becomes: Ni, Co>Mn>Ca, Mg>Sr>Ba. The effect of potassium on the demarcation current of muscle is inhibited not merely by Ca, but also by Sr, Ba, Co, Mn, and Ni ions, but not by Mg. Complex cobalt and chromium ions act like Ca when they are bi- or ter-valent, but not when they are univalent. Cu,  $\text{UO}_2$ , and Cd cannot replace calcium at all; Zn, Ni, and Ce ions can only do so partly.

J. C. D.

**Theory of Odour.** HANS HELLER (*Biol. Zent.*, 1919, 39, 364—370; from *Chem. Zentr.*, 1920, i, 139).—Chemical and physiological considerations lead the author to consider Teudt's theory (A., 1913, i, 607) untenable.

H. W.

**Polonium Radiation and Recovery of Function.** H. ZWAARDEMAKER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, 22, 383—385).—The effect of  $\alpha$ - or  $\beta$ -rays in restoring cardiac action (A., 1917, i, 241) appears to be due to the direct action of the rays, rather than to their influence in determining the liberation of potassium ions from the cardiac muscle. Thus the beating of a frog's heart, which had ceased owing to removal of potassium ions from the circulating liquid, was restored when the organ was exposed to  $\beta$ -rays from polonium, but ceased again when potassium ions were supplied in addition, owing to the opposing effects of  $\alpha$ - and  $\beta$ -rays (A., 1918, i, 326). It revived, however, when either the polonium or the potassium ions were removed.

J. K.

**Permeability of the Glomerular Membrane to Stereoisomeric Sugars.** H. J. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, 22, 351—359).—Previous investigations (A., 1919, i, 187) gave results which led the author to suspect that the retention of dextrose by the glomerular membrane was in some manner connected with the configuration of the sugar molecule.

The hypothesis that the group  $\begin{array}{c} \text{C}\cdot\text{OH} \\ | \\ \text{H}\cdot\text{C}\cdot\text{OH} \end{array}$  causes retention cannot be true, for *l*-arabinose and *l*-mannose pass through the kidney, whilst *d*-galactose, *l*-xylose, and *d*-ribose are partly retained. Of all the sugars examined (hexoses and pentoses) only dextrose is completely retained by the glomerular membrane.

J. C. D.

**The Partial Permeability of the Glomerular Membrane to *d*-Galactose and some other Multi-rotatory Sugars.** H. J. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, 22, 360—373).—The multi-rotatory sugars can be divided into three groups according to their behaviour in the kidney. The first group consists of those sugars of which both modifications are retained by the glomerular membrane. Of this class only one

representative, dextrose, is known. The second group (*d*-galactose, *d*- and *l*-xylose, and *d*-ribose) are partly diffusible through the renal glomerulus, and apparently only one modification is retained. The third class consists of sugars, both modifications of which pass the glomerulus, such are *l*-glucose, *d*-mannose, *d*- and *l*-arabinose. In the case of the members of the second group, the retention or non-retention is governed wholly by the positions which the H and OH linked to the asymmetric C-atom occupy relatively to each other. J. C. D.

**The Active Principles of the Pituitary Gland.** HAROLD WARD DUDLEY (*J. Pharm. Expt. Ther.*, 1919, **14**, 295—312).—The dried and powdered gland is extracted with acidified water, and the extract purified by precipitation with colloidal ferric hydroxide. From the filtrate, by continuous extraction with butyl alcohol under reduced pressure, crystalline fractions may be obtained which possess strong physiological activity. The extract contains all the uterine stimulant, together with some of the pressor substance and contaminating substances. The view expressed by Abel and Kubota (*A.*, 1919, **i**, 506) that histamine is identical with the uterine stimulant of the pituitary gland, is not confirmed. Considerable differences in the properties of these substances were observed. J. C. D.

**Influence of Temperature on Narcosis of Muscle and Nerve.** R. HÖBER (*Pflüger's Archiv*, 1919, **174**, 218—232; from *Physiol. Abstr.*, 1919, **4**, 184).—The depression of irritability of muscle and of conductivity in nerve by the action of various narcotics is increased by warmth and diminished by cold. The effects of potassium chloride, cocaine, and novocaine on muscular irritability are independent of temperature. The dependence of the partition coefficients of indifferent narcotics on temperature has no apparent relationship to their narcotic powers. J. C. D.

**Carcinolytic Organic Acids.** ERNST FREUND and G. KAMINER (*Wien. klin. Woch.*, 1919, **32**, 1105; from *Chem. Zentr.*, 1920, **i**, 135—136).—Normal serum and normal tissue contain a fatty acid compound which is able to destroy cancerous cells, and is to be regarded as the protective substance of normal cells; it is termed the "normal acid" by the authors. Cancerous serum and tissue show a lack of normal acid, and contain in its place an unsaturated fatty acid compound which behaves as a protective material to the cancerous cell; to this the name *carcinomic acid* is assigned. At least ten times as much normal as carcinomic acid is necessary for neutralisation. Since the preparation of considerable amounts of normal acid is a matter of difficulty (5 litres of serum yield 0.1 gram of acid), the authors have attempted to replace it by acids that can be synthesised. Under similar conditions, oxalic and malonic acids are inactive, succinic acid is active, glutaric, adipic, and pimelic acids are inactive, suberic acid is again active, whilst azelaic and sebacic acids have no action. These results and those

of other experiments lead to the conclusion that the methylene group has a distinct influence on carcinolytic activity. Actually, decane- $\alpha\kappa$ -dicarboxylic acid has the power of destroying cancerous cells. The minimal concentrations for succinic, suberic, and decane- $\alpha\kappa$ -dicarboxylic acids are about 0.05%, 0.01%, and 0.005% respectively; a parallelism thus appears to exist between increase in activity and number of  $C_2H_4$ -groups. In connexion with carcinomic acid, the protective action of sterically different fatty acids towards cancerous cells has been examined. Among isomeric acids, only those substances have a protective effect in which two carboxyl groups must be assumed to be in close proximity to one another and to a carbon atom.

H. W.

**Significance of Potassium in the Organism.** H. ZWAARDEMAKER (*Pflüger's Archiv*, 1918, **173**, 28—77; from *Physiol. Abstr.*, **4**, 80).—A summary and extension of previous work (see A., 1917, i, 241; 1918, i, 326, ii, 182) on the replacement of potassium by equiradio-quantities of other elements. Irradiation from without can replace the addition of other radio-active elements to nutritive fluids, and it is immaterial which rays are used for this, except that they cannot be used together effectively, as they are then biologically antagonistic. The equilibrium necessary for proper activity is altered by eosin and by calcium, and in the opposite direction, by fluorescein, and in summer it is immaterial whether the radio-active element which replaces potassium be present in ionic form or as a colloid complex. A frog's heart under the influence of uranium is incapable of giving extra systoles in response to electrical excitation.

J. C. D.

**Genesis of Thiocyanic Acid in Animals. VIII.** SERAFINO DEZANI (*Arch. farm. sper. sci. aff.*, 1919, **27**, 148—160. Compare A., 1919, i, 506).—With man and the dog, just as with the rabbit, ingestion of cauliflower is followed by more or less intense elimination of thiocyanic acid in the urine. The thiocyanogenetic substance of the cauliflower is found also in the white and green forms of *Brassica oleracea* L. var. *capitata*. This substance appears to belong to the group of so-called extractive substances, as it is neither a protein nor an amino-acid precipitable by phosphotungstic acid, nor a thiocarbimide, nor an organic sulphide. The extractive substances of flesh contain no thiocyanogenetic substances.

T. H. P.

**The Important Rôle of Preluciferin.** RAPHAEL DUBOIS (*Rép. pharm.*, 1919, [3], **30**, 289—291. Compare A., 1897, ii, 112; Harvey, A., 1917, i, 365; 1919, i, 299; this vol., i, 202, 203).—The author objects to the terms photogenin and photophlein for luciferase and luciferin. Luciferase is the enzyme and luciferin the substrate concerned in biochemical oxidations with the production of light; both are thermolabile. The luciferin is used up in the reaction which produces light; but a further supply may

be made by the action of another enzyme, coluciferase, on preluciferin, which is thermostable and quite probably is an albumose. If a solution containing both luciferase and coluciferase be kept at 65°, the luciferase is destroyed. The coagulum is removed from the solution by filtration; the filtrate is mixed with a boiled solution which contains preluciferin; no light is produced. On addition of a small crystal of potassium permanganate to this solution to take the place of the destroyed luciferase, light appears at once, since the coluciferase has made luciferin from the preluciferin. Photophelein may be used as a generic name for mechanical, physical, and chemical agents which favour, activate, or excite the reaction between luciferase and luciferin. Such agents are agitation in the presence of oxygen, dilution with aerated water, heat, compounds with an alkaline reaction (ammonia, sodium carbonate, alkaloids, amines), ethyl ether, etc.; these agents have no action on solutions in which potassium permanganate does not disclose a trace of luciferin.

CHEMICAL ABSTRACTS.

**Bioluminescence. XII. The Action of Acid and of Light in the Reduction of Cypridina Oxyluciferin.** E. NEWTON HARVEY (*J. Gen. Physiol.*, 1920, 2, 207—213. Compare this vol., i, 202, 203).—The addition of acid to a boiled extract of cypridina (oxyluciferin) causes the formation of a substance (luciferin), which will give light with luciferase. It would seem, however, that the action of bacteria, yeast, muscle cells, etc., on oxyluciferin must be due not entirely to their acid reaction, but to their reducing power as well. The processes which occur in this reaction are compared with the reduction of methylene-blue, and a scheme co-ordinating the various factors which influence this example of bioluminescence is advanced.

J. C. D.

**Behaviour of Benzoylpropionic Acid, Phenylethyl Alcohol, and Phenoxyacetic Acid in the Organism of Man and Dog.** H. THIERFELDER and E. SCHEMPF (*Pflüger's Archiv*, 1917, 167, 280—288; from *Physiol. Abstr.*, 1917, 2, 465).—The first-named keto-acid is reduced to a hydroxy-acid, and of this the *l*-form is largely excreted as such; a portion of it is further changed. The *d*-form is reduced to phenylbutyric acid, and thus is partly, by  $\beta$ -oxidation, converted into phenylacetic acid, which unites with glutamine. A small amount of the keto- or hydroxy-acid is probably excreted in union with glycine. Phenylethyl alcohol is oxidised to phenylacetic acid. Phenylacetaldehyde given subcutaneously is excreted as phenaceturic acid. Phenoxyacetic acid is not a metabolic product. Most of it is recoverable as such in the urine.

J. C. D.

**Pharmacological Action of Ketocineole.** GUIDO CUSMANO (*Gazzetta*, 1919, 49, ii, 228—232).—Similar chemical behaviour is shown by camphor and ketocineole, which differ in molecular structure only as regards the nature of the bridge uniting the tertiary

and quaternary carbon atoms. In their physiological effects, however, these two compounds exhibit differences. The psychomotor excitation produced in man and other mammals by camphor appears only in embryo on administration of ketocineole, and is mostly masked by symptoms in which depression of cerebral activity is prominent. The differences are more distinct in the case of the frog; here the initial curaric action of camphor which prevents the development of the convulsions observed in warm-blooded animals, is not produced by ketocineole. T. H. P.

**Influence of Temperature and Concentration on the Toxicity of Solutions, particularly of Electrolytes.** O. HARTMANN (*Pflüger's Archiv*, 1918, **170**, 585—645; from *Physiol. Abstr.*, 1918, **3**, 573).—In an extensive series of experiments on *Bosmina longirostris*, O.F.M., a member of the Cladocera, the effect on the duration of life at ten different concentrations of various acids, inorganic salts, organic salts, and alcohols was studied at temperatures of 0°, 13°, 18°, and 30°. Toxicity curves for the various concentrations and temperatures are figured. The toxicity concentration curve resembles more or less closely the adsorption isotherm of the various substances. The specific toxicity of the substances concerned is responsible for the form and the specific course of the curve. The osmotic pressure, however, tends to shorten life in the higher concentrations of the mildly toxic substances, and determines the acute bend above a certain critical concentration in the case of these curves. The diminishing toxicity of the anion and univalent cation series shows a close correspondence with the known series. The toxicity of the individual substances diminishes on dilution in varying degrees; those with similar or identical toxicity concentration quotients show little change in their relative position, whereas those with widely different quotients exhibit the greatest change in their relative toxicity on dilution. A similar formula for the temperature-toxicity curve is given, but its untrustworthiness is indicated by the variety of constants yielded at different temperatures. The relation of the absolute value of temperature-coefficient ( $Q_{10}$ ) and its peculiar progress were subjected to a very searching analysis. The very high values often observed at the maximum and minimum temperatures are due to complicated physiological changes in the living system, which are rapidly completed on changes at the temperatures in question. Owing to the very different temperature-coefficients and temperature-toxicity coefficients of the various substances, changes in toxicity occur at different temperatures; substances with similar temperature-toxicity quotients maintain their relative position in the series, whereas those with different quotients alter their relation on changes of temperature. The form of the toxicity-concentration curve is sometimes different for different temperatures, as higher temperatures usually determine a more gradual rise in the duration of life on dilution. Hence the adsorption formula constants will apparently be different at different temperatures. The value of the tempera-

ture-coefficient is also apparently influenced by the concentration of the experimental fluid. A general formula, including concentration, temperature, and duration of life, was constructed from the individual formulæ; its accuracy, however, is only approximate, and varies greatly for the various substances. J. C. D.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Butylene Glycol Fermentation of Sugar by *Bacillus anthracis*.** M. LEMOIGNE (*Compt. rend. soc. biol.*, 1919, 82, 984—986; from *Chem. Zentr.*, 1919, iii, 1018. Compare this vol., i, 122).—Fermentation of sugar by three different varieties of *B. anthracis* gave distillates containing a small amount of a reducing agent which yielded diacetylosazone with phenylhydrazine, and is therefore regarded as acetylmethylcarbinol;  $\beta\gamma$ -butylene glycol could not be detected. The phenomena are thus analogous to those observed with the *B. subtilis* group; whilst, however, in the latter case the  $\beta\gamma$ -butylene glycol collects in the cultures, it is immediately transformed by *B. anthracis* into lactic acid, and cannot be detected even as a transitory phase. The author is led to the conclusion that lactic acid and butylene glycol are intermediate products of the same process of fermentation which follows a different course with *B. anthracis* and *B. subtilis*.  
H. W.

**Cycloclastic Power of Bacteria. I. A Quantitative Aerobic Decomposition of Histidine by Bacteria.** HAROLD RAISTRICK (*Biochem. J.*, 1919, 13, 446—458).—The bacterial decomposition of histidine was followed by studying the fate of the nitrogen groups. *B. paratyphosus* A, *B. paratyphosus* B, *B. faecalis alcaligenes*, and *B. pyocyaneus* can produce ammonia from both the amino-group of the side-chain and from the iminazole nucleus of the histidine molecule. With *B. proteus vulgaris* ammonia is formed only from the side-chain nitrogen, and it appears probable that this organism cannot break down the ring structure.

J. C. D.

**Respiratory Process of Nitrifying Bacteria. III. The Respiration of the Nitrite Organisms and the Influence of Chemical Substances.** O. MEYERHOF (*Pflüger's Archiv*, 1917, 166, 240—280; from *Physiol. Abstr.*, 1917, 2, 207).—The material used was obtained from a pure culture of *Nitrosomonas*, and Winogradsky's solution was employed as a culture medium.

Under favourable conditions cultures were obtained which in twenty-four hours could oxidise 4 grams of ammonium sulphate per litre to nitrite. The rate of respiration depends on the concen-

tration of the ammonium salt, the optimum being at a concentration of  $N/200\text{-NH}_4$ , whilst it is zero in a concentration of  $N/10\text{-NH}_4$ . The accumulation of the nitrite ion retards respiration, and growth stops when the concentration of this ion reaches  $0.25N$ . With decreasing partial pressure of oxygen there is decreasing respiration from about one-third atmospheric pressure downwards. The H-ion concentration strongly influences the respiration rate; the optimum is in a concentration of  $P_H=8.4$  to  $8.8$ ; outside the limits  $P_H=9.4$  and  $P_H=7.6$  no respiration takes place.

The rate of respiration is very sensitive to alkali and alkaline-earth salts, and the heavy metals are very toxic. Respiration and growth respond differently towards nitrogen-free organic substances. Dextrose retards growth in  $0.001M$ -solution, but respiration is not retarded in  $0.2M$ . Methyl alcohol is more toxic than ethyl alcohol.

J. C. D.

**The Free Energy of Biological Processes.** GEORGE A. LINHART (*J. Gen. Physiol.*, 1920, **2**, 247—251).—From considerations of energy exchange it is concluded that only about 1% of the total available energy is utilised in the fixation of nitrogen by *Azotobacter*, growing in a  $0.1$  molar solution of mannitol.

J. C. D.

**Nitrogen Metabolism in *Saccharomyces cerevisiae*.** LESLIE HERBERT LAMPITT (*Biochem. J.*, 1919, **13**, 459—486).—Excess of yeast ensures the removal of the greatest total amount of nitrogen. During active fermentation, the greater the coefficient of multiplication, the greater the amount of nitrogen assimilated by each cell. Active reproduction may result in a lowering of the nitrogen coefficient, but the final coefficient is independent of the initial value, tending to reach a constant value for any particular conditions of reproduction. The action of yeast on asparagine may result in the production of malic acid, the ammonium salt of which is readily fermented, with the production of ethyl alcohol. Propionic acid and its ammonium salt are not fermented (compare Effront, A., 1908, i, 491; 1909, ii, 255). Fermentative activity is essential to nitrogen assimilation, but, once induced, the deamination may continue after zymatic activity ceases. During fermentation, yeast loses nitrogen to the medium. This process, which has been termed "nitrogen excretion," is dependent on the life of the cell, and takes place even when nitrogen is being assimilated. The substances which are excreted can be used as a source of nitrogen by the yeast under suitable conditions. Increase in the amount of sugar available increases the rate of excretion, but there is no proportion between zymatic activity and such excretion.

J. C. D.

**Influence of Substances Extracted from Yeast on the Fermentation of Carbohydrates by Yeast.** EMIL ABDERHALDEN (*Fermentforsch.*, 1919, **3**, 44—70; from *Chem. Zentr.*, 1920, i, 16. Compare Abderhalden and Schaumann, A., 1919, i, 108).—The influence of yeast extract is proved in a series of

experiments in which equal amounts of yeast are allowed to act on equal weights of carbohydrate, and fresh amounts of the latter are added as soon as the evolution of carbon dioxide markedly slackens until further addition does not cause renewed fermentation; in these circumstances, much more sugar is fermented in the presence of alcoholic yeast extract than is otherwise the case. Simultaneously, the rate of fermentation is greatly increased, generally to a considerably greater extent than by fructosediphosphoric acid. The yeast cells also increase more rapidly, but the greater activity which is thus indicated is not sufficient to account entirely for the action of the yeast extract, since the activating effect is also observed when expressed juice or dry yeast is used. H. W.

**Observations on Yeast (mainly Munich Brewery Press Yeast).** T. BOKORNY (*Pflüger's Archiv*, 1916, 164, 203—273; from *Physiol. Abstr.*, 1916, 1, 453).—In keeping with the fact that sucrose is more readily fermented than dextrose, the previous treatment of yeast with antiseptics destroyed its capacity to ferment the latter, but not the former sugar or maltose. Glycerol may be included among the adequate sources of carbon for the growth of yeast. When added to a nutrient medium containing sugar, ammonium sulphate, and salts, an increase of 30 to 42% in the dried weight was observed at the end of three days, as compared with 9% in the control culture. The substitution of peptone or amino-acids for the ammonium salt gave similar results. Although the capacity of furnishing the aldehyde atom-complex is probably the determining factor in the utilisation of carbon, formaldehyde and other aldehydes were not assimilated by the yeast cell.

Peptone is an excellent source of nitrogen, and its addition to a medium containing sugar and salts resulted in an increase of 163% in the dried weight after the lapse of three days; glycine was the least satisfactory of the amino-acids examined, and yielded an increase of only 19%.

Although large quantities of fat have been found in involuting yeast, no appreciable increase in the fat content occurred even when yeast was cultivated in the most favourable medium (peptone and sugar solution).

The study of certain injurious factors showed that yeast was not destroyed by freezing or by drying at the ordinary temperature for eight days; prolonged drying killed the yeast, but did not destroy the zymase. Neutral salts in saturated solution usually prevented fermentation within a few days. The injurious effects of a number of organic and inorganic acids, both on the cell and on zymase activity, are recorded. J. C. D.

**The Chemistry of Alcoholic Fermentation.** ERNST ZERNER (*Ber.*, 1920, 53, [B], 325—334).—The author gives an account of the manufacture of glycerol by the Connstein-Lüdecke process (A.,

1919, i, 463) during the war in Austria-Hungary, which is also of interest, since some of the conclusions are at variance with those arrived at by Neuberg and Reinfurth (this vol., i, 125). The most important results are as follows. Equivalent amounts of glycerol and acetaldehyde are produced in the process; in addition, alcohol and carbon dioxide are formed, and these are the only substances obtained in appreciable amount. Increase in the amount of sodium sulphite increases the yield of glycerol and acetaldehyde, but more than 38% of glycerol cannot be obtained. Sodium sulphite may be replaced by sodium hyposulphite. Failure to produce glycerol in quantitative amount by sufficiently increasing the relative proportion of sulphite has been attributed by Neuberg to dissociation of the aldehyde-bisulphite compound; this conclusion appears to be unfounded, since with moderate additions of sulphite the equivalent amount of glycerol is almost obtained, whilst with very large additions (which should have the effect of suppressing dissociation of the aldehyde-bisulphite compound) the yield of glycerol sinks to about two-thirds of that theoretically possible. The effect seems rather to be attributable to the fact that action between aldehyde and bisulphite is not an instantaneous process, and that a certain amount of opportunity is thus offered for further degradation of the aldehyde and glycerol to alcohol and carbon dioxide.

At first sight, it seems reasonable to suppose that pyruvic acid is an intermediate stage in the fermentative conversion of sugar into aldehyde and glycerol, and Neuberg has shown that the acid can actually be fermented in the presence of sulphite. In these experiments, he has only used one-eighth to one-fourth the equivalent amount of the sulphite; the use of larger proportions, however, shows that the bisulphite compound of pyruvic acid is not fermentable, and that neither pyruvic nor glyceric acid can constitute the intermediate stage in the production of aldehyde by alcoholic fermentation.

When sugar is fermented in the presence of sodium thiosulphate, sulphur is soon precipitated, hydrogen sulphide is evolved, and, after a time, fermentation ceases; the yield of glycerol, reckoned on the sugar actually fermented, is very considerable. When the experiments are repeated with the addition of sodium sulphite or sodium hydrogen carbonate, reaction proceeds as if the thiosulphate were not present. It appears, therefore, that an acid is produced during fermentation which decomposes the thiosulphate according to the equation  $\text{Na}_2\text{S}_2\text{O}_3 + \text{HX} = \text{NaHSO}_3 + \text{NaX} + \text{S}$ . The sulphur is converted into hydrogen sulphide by the reducing action of the yeast, whilst the sodium hydrogen sulphite combines with the aldehyde, and thus provides the possibility of a good yield of glycerol. Fermentation is stopped owing to the production of organic sulphur derivatives, which poison the yeast. In the presence of sulphite or carbonate, the acid is neutralised by these, and the thiosulphate remains undecomposed. Generally, it may be stated that glycerol and aldehyde are intermediate products of

alcoholic fermentation which are simultaneously formed, and, in normal circumstances, simultaneously disappear; as a preliminary phase, an acid must be formed, which, however, is not identical with pyruvic acid.

During normal fermentation (without sulphite), the maximum amount of aldehyde appears to be present in the middle period of action.  
H. W.

**The Regulator System: Primary Phosphate-Bicarbonate-Free Carbonic Acid, in place of the System: Primary Phosphate-Secondary Phosphate.** W. WINDISCH and W. DIETRICH (*Woch. Brau.*, 1920, **37**, 81—83).—The lowering of surface tension of aqueous solutions of eucupine dihydrochloride, which results from the liberation of the free base by alkalis (compare Traube, A., 1915, ii, 571), has been used as a means of investigating the equilibrium in the reaction  $K_2HPO_4 + CO_2 = KH_2PO_4 + KHCO_3$  in dilute aqueous solutions. It is concluded that in presence of excess of carbon dioxide the reaction proceeds practically to completion from left to right. In living and breathing tissues, therefore, and in fermenting liquids, phosphates must be present entirely as primary salts in equilibrium with potassium hydrogen carbonate and carbon dioxide. Only when respiration or fermentation has ceased and there is no longer an excess of carbon dioxide can dipotassium phosphate exist in equilibrium with the monopotassium salt.  
J. H. L.

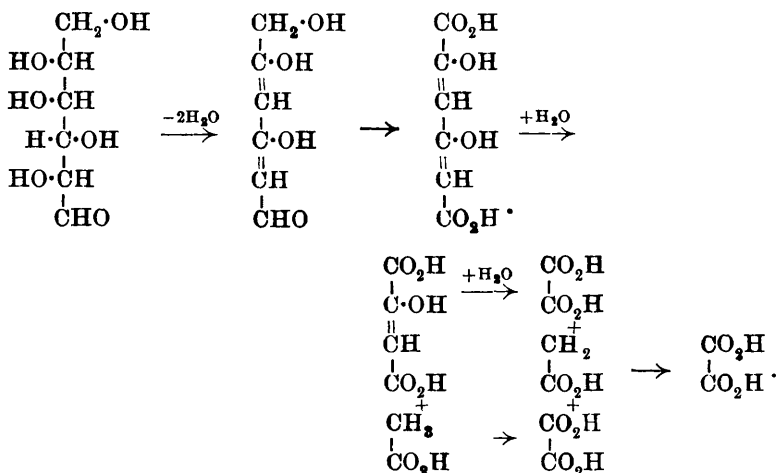
**Mechanism of the Formation of Oxalic Acid by *Aspergillus niger*.** HAROLD RAISTRICK and ANNE BARBARA CLARK (*Biochem. J.*, 1919, **13**, 329—344).—Good yields of oxalic acid were obtained when *Aspergillus niger* was grown in the presence of the four-carbon dibasic acids, this being especially true in the case of succinic, fumaric, and malic acids. Very little oxalic acid was produced from sodium maleate, a result which is in agreement with Buchner's observation that *A. niger* can utilise fumaric acid, but not maleic acid, as a source of carbon.

When the four-carbon monobasic acids were examined, there was very little growth of the mould and no production of oxalic acid.

Unexpected results were obtained in the case of the three-carbon acids. In almost all cases there was good growth of the organism, but practically no production of oxalic acid. Of the two-carbon acids, acetic acid behaved differently from glycollic and glyoxylic acids in giving rise to a considerable production of oxalic acid.

Growth of *A. niger* was good in media containing formic acid, but no production of oxalic acid was apparent. A consideration of these results leads the authors to conclude that the breakdown of the sugar molecule by *A. niger* does not take place by a primary splitting of one molecule of sugar into two molecules of a three-carbon acid. Neither can it occur as a gradual breakdown of the molecule carbon by carbon, for this would not give rise to the large yields of oxalic acid unless the micro-organism can synthesise this

acid from one-carbon compounds, and the authors present evidence that this does not occur. The decomposition probably takes place in two stages, and may be illustrated by the following scheme:



The evidence in support of these changes is discussed. J. C. D.

**Colloidal Chemistry of Cell Division.** JOSEF SPEK (*Koll. Chem. Beihefte*, 1920, 12, 1—91).—A number of experiments on the effect of salts of lithium, potassium, magnesium, and calcium on the cell division of *Paramœcium caudatum*, *P. aurelia*, and *Stylonichia mytilus* are described. It is shown that salts can either delay or accelerate the cell division by changing the swelling conditions of the colloidal plasma, or they can hinder the division by accumulating in the inside of the cells. Salts which have a very strong influence on the swelling of colloids are also capable of effecting a marked change in the velocity of cell division. Salts which have two ions, each possessing a strong swelling action, accelerate the rate of cell division to a marked extent. Such salts as lithium bromide, lithium chloride, and potassium thiocyanate possess this property to a marked degree. That these salts accelerate the plasma swelling of the *Paramœcia* is seen by the increase in volume of the organisms. Salts which reduce the swelling, such as calcium chloride and the sulphates, retard the cell division to a marked extent. The sulphates increase in their retarding action in the order  $\text{Li} > \text{K} > \text{Na}$ . In the case of lithium sulphate, it is possible that the accelerating influence of the cation may outweigh the retarding influence of the anion. In the case of the chlorides, the influence of the cations follows the order  $\text{Li} > \text{Na} > \text{Ca}$ , which is the same as the order in which they produce swelling. Potassium chloride, which accelerates the swelling of *Paramœcia* more strongly than sodium chloride, has a much less effect than lithium chloride and potassium thiocyanate, and sometimes it retards the cell division. This is explained by the greater

ease with which this salt passes inside the cells, or, in other words, it is due to a too large increase in salt content of cells in media containing potassium chloride. Sodium chloride has much less power of penetrating the cell wall. The very powerful action of lithium chloride and potassium thiocyanate is due to their coagulating influence on the surface of the cell body without affecting the interior of the cell. In the case of magnesium salts, both the chloride and the sulphate have a very indifferent action, which is due to a slight penetration of the salt. No single experiment points to cell division being effected by the withdrawal of water, that is, cell division is not an osmotic phenomenon. The addition of a substance, capable of swelling, to the culture medium, for example, gelatin, retards the cell division. Different species of *Paramœcia* behave differently towards salts. The difference is attributed to varying permeability of the cells and a dissimilar swelling capacity of the plasma. The experimental results lead to the following hypothesis. The swelling of the plasma colloids, before the cell division, is brought about by the appearance of a base, which is a by-product in the synthesis of the nuclein. The increased permeability during the cell division is accompanied by an increase in the salt content of the cell which compensates the action of the base. An increase in the salt concentration above a given quantity stops the cell division. The formation of substances possessing good swelling properties in the cell occasions new cell division. The swelling of the colloids promotes the gas exchange and the hydrolytic processes in the cell. Every cell division leads more or less completely automatically to further cell divisions.

J. F. S.

**The Glycerophosphatase of Seeds.** ANTOINE NĚMEC (*Bull. Soc. chim.*, 1920, [iv], **27**, 153—158).—The author has recently shown (this vol., i, 268) that glycerophosphatase is very widespread in plant cells and in the tissues of ungerminated seeds. It is now shown that this enzyme acts best in an acid medium, the optimum action being obtained with an acidity of approximately 0.06*N*. The velocity of the action which the enzyme produces indicates that it is a bimolecular action.

W. G.

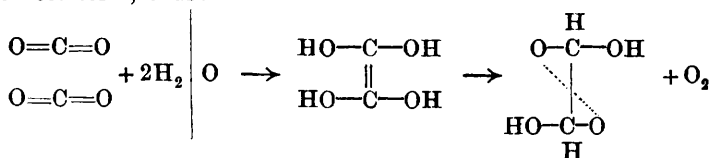
**The Assimilation Problem.** GERTRUD WOKER (*Pflüger's Archiv*, 1919, **176**, 11—38; from *Chem. Zentr.*, 1920, i, 90).—Carbon dioxide is a very inert substance, and, in its ordinary form, is only very slightly attacked by reducing agents. If reaction is to occur, it is necessary for it to suffer change in its molecular structure. "This probably occurs by isomerisation, with the formation either of a primary peroxide,  $C \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$ , or of a secondary peroxide,  $C \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$ , which, by addition of water, yields  $C \begin{smallmatrix} \diagup O-OH \\ \diagdown OH \end{smallmatrix}$ ." It

is found that bicarbonates and carbonates at the moment of their production or disappearance are more reactive than the ordinary

salts. A yellow coloration is produced when a mixture of potassium and sodium hydrogen carbonates and the corresponding normal carbonates in the presence of methyl alcohol is exposed to intense sunlight; the solution reduces Fehling's solution, but the presence of sugar could not be established. The corresponding carbonates and hydrogen carbonates alone do not behave in a similar manner. According to the author, assimilation is made up of a reduction phase and a subsequent combination phase. Assuming the occurrence of isomerisation and the formation of a secondary peroxide,  $>C\begin{smallmatrix} O \\ \diagup \\ OH \end{smallmatrix}$ , a compound is formed which tends to eliminate oxygen, and thereby to yield the group  $>CH\cdot OH$ , which is predisposed towards condensation. "Assuming the formation and immediate further utilisation of the unsaturated radicle  $>CH\cdot OH$  (which is tautomeric with formaldehyde), a number of difficulties inherent to Baeyer's formaldehyde hypothesis are circumvented without losing the advantages of the latter." The formation of formaldehyde or its desmotope from methyl alcohol and carbon dioxide can, in the presence of excess of the latter, lead to the production of dihydroxyacetone, which may be of importance for the synthesis of sugars, and, by reduction, for the formation of glycerol. Reductions with methyl alcohol are of considerable interest, since the latter is widely distributed in nature and chlorophyll is an ester of methyl alcohol. The author shows, further, how the following substances may arise by the union of  $>CH\cdot OH$  groups in the "condensation-phase": dextrose, lævulose, inositol, the  $\gamma$ -pyrone ring, furfuraldehyde, pyrogallol, quinol, etc. The same group can also react with ammonia, possibly derived from formhydroxamic acid, to yield the alkaloids of the pyrrolidine or piperidine series. The rôle of chlorophyll in assimilation is discussed, the author assuming that it sensitises the isomerisation of the carbon dioxide and acts as a catalyst in the condensation phase; an intermediate union of the  $>CH\cdot OH$  group with the magnesium atom of the chlorophyll appears most probable, and explains the formation of optically active substances from initially inactive material, since union occurs with an asymmetric substance, namely, the chlorophyll dye.

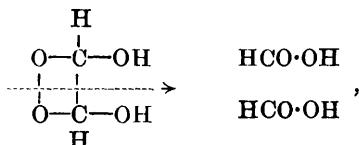
H. W.

**New Theory of Carbon Dioxide Assimilation.** P. R. KÖGEL (*Zeitsch. wiss. Photochem.*, 1920, **19**, 215—223).—A theory of the assimilation of carbon dioxide by plants is put forward. The action of light is to polymerise the carbon dioxide, which with hydrogen then forms tetrahydroxyethylene, which passes over into the keto-form, thus:

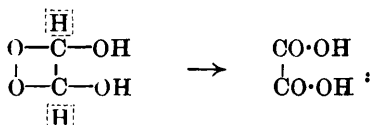




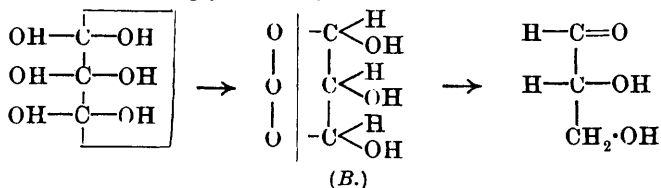
This compound contains the characteristic sugar grouping  $\text{HO}-\overset{\text{H}}{\text{C}}-\text{O}$ . The formation of the plant acids, formic and oxalic, is easily deduced from diketoethyl dioxide. In the case of formic acid, it is a simple splitting of the molecule,



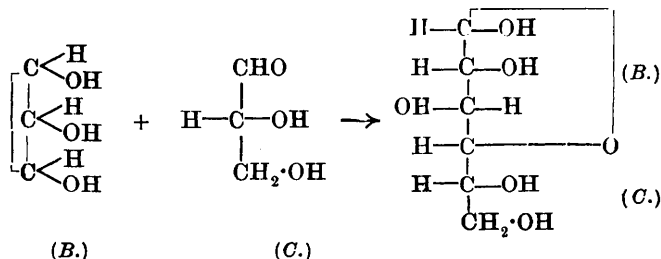
whilst in the case of oxalic acid the removal of two hydrogen atoms is necessary.



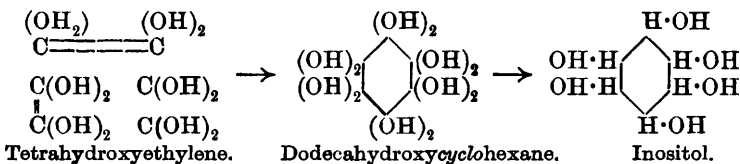
If, instead of two molecules of carbon dioxide, three undergo photopolymerisation, then glyceraldehyde is produced,



and the glyceraldehyde combines with B, with the loss of three oxygen atoms, to form dextrose.



The formation of inositol on this hypothesis is represented as follows:



J. F. S.

**The Absorption of Calcium by the Roots of Plants and its Antitoxic Properties with respect to Copper.** L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1920, 170, 420—425. Compare A., 1917, i, 530).—Calcium, even in excess, does not prevent the absorption of copper by the roots of plants or its diffusion into their aerial organs. Similarly, copper does not prevent the assimilation of calcium. The poisonous effect of copper is not due, therefore, to its depriving the young plant of one of its essential nutrients. The antitoxic action of calcium with respect to copper is physiological, and not due to its preventing the penetration of the metal. The explanation probably lies in the fact that the calcium favours the evolution of the plant, giving it greater vigour, and in particular giving it greater volume, into which the copper diffuses, thus preventing, within certain limits, all dangerous accumulation of this latter metal. W. G.

**Some Factors Affecting the Concentration of Electrolytes in the Leaf Sap of *Syringa vulgaris*.** T. G. MASON (*Sci. Proc. Roy. Dubl. Soc.*, 1919, 15, 651—666. Compare Dixon and Atkins, A., 1916, i, 108).—The determination of the concentration of electrolytes of the cell by means of conductivity observations is unsatisfactory unless allowance is made for the viscosity of the sap, and to this extent Chandler's results (compare *Missouri Agric. Exp. Stat. Res.*, 1914, *Bull.* No. 14) are incorrect. The application of the linear viscosity correction as a means of ascertaining the quantity of electrolytes in the sap is liable to be misleading, and recourse must be had to ascertaining the loss in conductivity which takes place in some salts, such as potassium chloride, after solution in the sap.

Considerable fluctuations in the concentrations of electrolytes in the leaf sap of *Syringa vulgaris* trees growing in different localities have been found. There appears to be a general tendency for the concentration of electrolytes to vary inversely with that of the non-electrolytes. It is suggested that these fluctuations are associated with the rate of carbon assimilation, which determines the rate at which electrolytes are removed from solution in metabolism. It is shown that the concentration of salts in the ascending sap is not responsible for these fluctuations. W. G.

**Fat-soluble Vitamine. IV. The Fat-soluble Vitamine Content of Green Plant Tissues, together with some Observations on their Water-soluble Vitamine Content.** H. STEENBOCK and E. G. GROSS [with co-operation of MARIANA T. SELL] (*J. Biol. Chem.*, 1920, 41, 149—162. Compare this vol., i, 274).—Five % of clover or lucerne as the sole source of fat-soluble accessory factor in the diet of a rat will permit normal growth and reproduction. Lettuce, spinach, and chard contain the accessory factor in amounts of the same order, but, of these, lettuce appears to be the poorest. In harmony with the theory that fat-soluble A is associated with certain yellow plant pigments is the fact that

cabbage does not contain much of the accessory factor (*loc. cit.*). Fifteen % of lucerne, clover, and cabbage supplied sufficient water-soluble *B* for growth of young rats. J. C. D.

**Fat-soluble Vitamine. V. Thermostability of the Fat-soluble Vitamine in Plant Materials.** H. STRENBÖCK and P. W. BOUTWELL [with co-operation of MARIANA T. SELL and E. G. GROSS] (*J. Biol. Chem.*, 1920, **41**, 163—171).—The fat-soluble vitamine in yellow maize is apparently unaffected by heating three hours under 7 kilos. pressure. Neither does this treatment cause appreciable destruction of the factor as found present in chard, carrots, sweet potatoes, or squash.

No deleterious action of the ensiling process on the fat-soluble accessory factor was detected. The experiments indicate that the accessory substance, as it occurs in grains, leaf and stem tissue, fleshy roots, and curcubitous vegetables, is comparatively thermostable. J. C. D.

**The Ability of Plants to Form Optical Antipodes.** KUET HESS and WILHELM WELTZIEN (*Ber.*, 1920, **53**, [B], 119—129).—See this vol., i, 328.

**Occurrence of Chlorogenic Acid in Araliaceæ and Gorter's Reaction.** A. W. VAN DER HAAR (*Pharm. Weekblad*, 1920, **57**, 194—195).—Leaves of ordinary ivy (*Hedera helix*) and of various members of the *Araliaceæ* were tested for the presence of chlorogenic acid by the method given by Gorter (*A.*, 1909, i, 588). Ivy leaves alone gave a faint positive reaction; the others gave no reaction. The *Araliaceæ* examined were of European growth; those which Gorter found to contain chlorogenic acid were obtained from the East Indies (*A.*, 1909, i, 935). W. S. M.

**Origin and Transformation of Inulin in Artichoke Tubers.** H. COLIN (*Bull. Assoc. Chim. Sucr.*, 1919, **37**, 121—126).—The leaves of the artichoke (*Helianthus tuberosus*) are free from inulin at all stages of growth. They contain sugars and starch, and are as rich in starch as the leaves of the potato plant. Formation of inulin takes place in the stem, throughout its whole length, and is completed in the tubers. The inulin must be produced chiefly from dextrorotatory carbohydrates supplied by the leaves. There is practically no difference between young and mature tubers in respect of the nature of the carbohydrates present. The rotatory power of the juice of the tubers undergoes no appreciable change between August and November, but afterwards approaches zero, and finally becomes positive, owing to the conversion of inulin into levosans of lower molecular weight and the formation of sucrose. When the new plant begins to develop, the inulin passes into the stem chiefly in the form of reducing sugars. J. H. L.

**Fatty Acids of Earthnut Oil.** A. HEIDUSCHKA and S. FELSER (*Zeitsch. Nahr. Genussm.*, 1919, **38**, 241—265).—The fatty acids

obtained from a specimen of earthnut oil had the following composition: arachidic acid 2·4%, lignoceric acid 1·9%, stearic acid 4·5%, palmitic acid 4·0%, oleic acid 79·9%, and linolic acid 7·4%. The oleic acid probably included a small quantity of hypogæic acid. W. P. S.

### **Cyanogenesis in Sudan Grass: a Modification of the Francis-Connell Method of Estimating Hydrocyanic Acid.**

PAUL MENAUL and C. T. DOWELL (*J. Agric. Res.*, 1920, 18, 447—450).—A determination was made of the amount of hydrocyanic acid in Sudan grass in freshly-cut samples at intervals of a week during the season. The amount obtained was found to be 0·0105% in the fresh plant, only a third of that contained in the grain sorghums. The amount was determined by finely dividing the grass and leaving it with water at 40° for two hours. After this it was made strongly acid with tartaric acid, and distilled into 30 c.c. of 2% sodium hydroxide. The cyanide was precipitated as Prussian-blue, which was burned in a muffle furnace and weighed.

The colorimetric method of Francis and Connell for the estimation of hydrocyanic acid (A., 1913. i, 1284) was investigated and improved, as follows. The distillate containing the hydrocyanic acid is evaporated with 1 c.c. of concentrated yellow ammonium sulphide at 70°. The residue is heated at 130°, dissolved in 10 c.c. of warm water acidified with hydrochloric acid, and calcium chloride solution added drop by drop until the sulphide ceases to form; then 10% ferric chloride solution is added until the red colour is permanent. The solution is then filtered, and 5 c.c. of ferric chloride solution added to the filtrate. The heating at 130° is found to prevent colloidal sulphur going into solution, and the addition of the second quantity of ferric chloride produces the maximum intensity of colour. No change in this intensity is produced by the addition of electrolytes. A standard solution was prepared from a standard solution of potassium cyanide in a similar manner, and the two solutions were compared in a Bock-Benedict colorimeter. J. H. J.

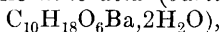
**Hydrocyanic Acid Content of *Phaseolus lunatus*.** H. LÜHRIG (*Chem. Zeit.*, 1920, 44, 166—167).—Beans of the *Phaseolus lunatus* species were found to yield small quantities of hydrocyanic acid when steeped for several hours in water, then macerated, acidified with tartaric acid, and steam distilled. The distillate was collected in dilute silver nitrate solution, and since sulphur compounds also distilled, it was found necessary to dissolve the silver cyanide in ammonia, separate the silver sulphide by filtration, and reprecipitate the silver cyanide by the addition of nitric acid. The silver cyanide was then collected, ignited, and the residue of metallic silver weighed. Nine samples of the beans examined yielded from 5·1 to 23·4 mg. of hydrocyanic acid per 100 grams of beans. The beans did not produce any poisonous effect when eaten in large quantity, provided that they had been

properly steeped in water, washed, and boiled for three hours. Treatment with emulsin during the steeping operation did not increase the amount of hydrocyanic acid yielded to any appreciable extent.

W. P. S.

### Constituents of the Seeds of *Pharbitis nil chois*.

Y. ASAHINA and S. X. TERADA (*J. Pharm. Soc. Japan*, 1919, **452**, 821).—From the seed of *Pharbitis nil chois* (*P. hederacea chois*, *P. triloba*, Miq., *Ipomea triloba*, Th.) (the Chinese drug "Ch'ien-niu-tzu"), the authors have isolated 3.44% of the resin glucoside pharbitin, m. p. about 145—155°, darkening at 134°,  $[\alpha]_D^{25} - 43.53^\circ$  (acetyl derivative, m. p. 115—120°, softening at 110°,  $[\alpha]_D^{25} - 18.87^\circ$ ), which yields by hydrolysis (1) a fatty acid which is volatile with steam (possibly a valeric acid with some tiglic acid), (2) the non-volatile *nilic acid* (barium salt,



and (3) pharbitic acid, m. p. 155—162°,  $[\alpha]_D^{25} - 47.61^\circ$  (Kromer, A., 1897, ii, 68, gives m. p. 156—162° and  $[\alpha]_D - 46.62^\circ$ ). The hydrolysis of pharbitic acid by 5% sulphuric acid yields dextrose, a pentose (osazone, m. p. 172°; possibly methylpentose), and an acid identical with ipurolic acid obtained by Power and Rogerson from *Ipomea purpurea* (A., 1908, ii, 725).

### CHEMICAL ABSTRACTS.

### Chemical Constituents of Malt Germs, especially Hordenine.

YOSHITAKA HASHITANI (*J. Tokyo Chem. Soc.*, 1919, **40**, 647—667).—The air-dried germs contain water 10.21, ash 3.02, crude protein 21.49, pure protein 13.32, crude fat 3.19, crude fibre 18.40, soluble non-nitrogenous substances 43.69, reducing sugar (calculated as dextrose) 3.65, non-reducing sugar 1.02, pentosan 18.42, methylpentosan 1.05, and cellulose 12.04%. The cell wall is shown by microchemical examination to contain mainly cellulose, which, after hydrolysis with 3% sulphuric acid, responded with tests for xylose, dextrose, lævulose, and galactose. The dried malt germ contains 4.65% of nitrogen. Of the total nitrogen, 6.67% corresponds with water-soluble protein nitrogen, 56.77% with pure protein nitrogen, 20.22% with amino-acid nitrogen, 23.01% with diamino-acid, purine base, and other nitrogen. The air-dried material contains 0.11 of asparagine and 0.13% of hordenine. The sulphate of the latter forms colourless needles, m. p. 209—211°; the hydrochloride has m. p. 176.5—177.5°, the hydrobromide m. p. 173—174°, the hydrogen tartrate m. p. 170—171°, the normal tartrate m. p. 180—181°, the hydriodide m. p. 227—228°, and the methiodide m. p. 179—180°. Benzoyl-hordenine, m. p. 47—48°, forms a hydrobromide, m. p. 171—172°, and a sulphate, m. p. 270—271°.

Alcoholic fermentation is accelerated by the addition of 0.005%, but is stopped completely by 1.28% of hordenine.

### CHEMICAL ABSTRACTS.

## Organic Chemistry.

**The Electronic Constitution of Normal Carbon Chain Compounds, Saturated and Unsaturated.** EUSTACE J. CUY (COUYUMDJOPOULOS) (*J. Amer. Chem. Soc.*, 1920, **42**, 503—514).

—A theory of the constitution of carbon chain compounds is put forward, based on the conceptions of Hanke and Koessler (A., 1919, i, 4). Two assumptions are made: first, that carbon compounds are polar in character, and, secondly, that carbon atoms in a chain tend to assume alternately positive and negative charges, and it is shown how, by these assumptions, the alternating character of many physical properties in homologous series, for example, the melting points in the fatty acid series, can be accounted for. Further evidence in support of the hypothesis is derived from a consideration of the manner of addition of

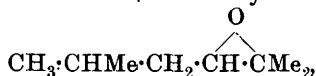
hydrogen haloids to unsaturated carbon compounds. The electronic formula for propylene, for example, is as annexed; the most hydrogenated carbon atom is electronegative; the adjacent carbon atom is electropositive, and combines with the electronegative halogen (Markovnikov's rule). A number of exceptions to this rule, Ipatiev's rule for the addition of hydrogen bromide to compounds of the type  $R_2C=C-CH_2$ , and the isomeric rearrangement of alkyl haloids are accounted for by the hypothesis.

E. H. R.

**Condensations of *n*-Butyl Alcohol and *n*-Butaldehyde** CHARLES WEIZMANN and STANLEY FREDERICK GARRARD (T., 1920, **117**, 324—338).

**The Walden Inversion.** II. P. KARRER and W. KAASE (*Helv. Chim. Acta*, 1920, **3**, 244—251. Compare A., 1919, i, 570).—The action of hydrochloric acid on isobutylene oxide results in the formation of  $\gamma$ -chloro- $\alpha$ -methylpropan- $\beta$ -ol, accompanied by an isomeride, which Michael considered to be  $\beta$ -chloro- $\alpha$ -methylpropan- $\gamma$ -ol. There is, however, no positive evidence in favour of this view (Krassusky, A., 1907, i, 459), but confirmation of it is now brought forward.  $\gamma$ -Chloro- $\beta\epsilon$ -dimethylhexan- $\beta$ -ol,  $CH_3\cdot CHMe\cdot CH_2\cdot CHCl\cdot CMe_2\cdot OH$ , obtained by the action of magnesium methyl iodide on ethyl  $\alpha$ -chloro- $\gamma$ -methylvalerate, is a clear oil, b. p.  $77^\circ/12$  mm., with an odour resembling that of turpentine,

and has  $[\alpha]_D^{25} -57.2^\circ$  in alcohol. By treatment with potassium hydroxide, it is converted into  $\beta\epsilon$ -dimethylhexene- $\beta\gamma$ -oxide,



b. p. 134—136°,  $[\alpha]_D^{18} +8.97^\circ$  in alcohol under ordinary pressure, or 46°/17 mm., a clear liquid with a refreshing, fruity odour. It reacts instantly with cold concentrated hydrochloric acid. Although the product boils at 77°/13 mm., and has the same odour as the above chlorodimethylhexanol, it has  $[\alpha]_D^{18} +14.15^\circ$  in alcohol, and must therefore contain a certain proportion of the isomeric  $\beta$ -chloro- $\beta\epsilon$ -dimethylhexan- $\gamma$ -ol. The possibility that the production of the mixture is due to a Walden inversion is excluded by the fact that it regenerates the above oxide when treated with potassium hydroxide. The paper concludes with comments on Clough's reply (this vol., i, 368).

J. K.

**Preparation of Ethylene Glycol.** CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 300122; from *Chem. Zentr.*, 1920, ii, 241).—Ethylene is oxidised with permanganate solution in such a manner that (1) contact of the glycol formed with the permanganate is avoided as far as possible, as, for example, by adoption of the counter-current principle, and (2) accumulation of manganese mud or other products which might retain the glycol in the reaction vessels is obviated. The yields are nearly quantitative. Technical ethylene, such as that obtained by the catalytic hydrogenation of acetylene, and therefore always containing a certain amount of impurities, of which the chief is ethane, may be advantageously used. The ethane is then obtained as by-product.

H. W.

**The Preparation of Halogenohydrins.** JOHN READ and MARGARET MARY WILLIAMS (T., 1920, 117, 359—362).

**Preparation of Pinacone.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 306304; from *Chem. Zentr.*, 1920, ii, 445).—Acetone is reduced electrolytically in acid solution in the presence of metallic salts, which inhibit its conversion into more completely reduced products, such as isopropyl alcohol. Salts of bismuth, mercury, manganese, nickel, antimony, silver, and iron are found to be particularly suitable for this purpose.

H. W.

**Preparation of Pinacone Chlorohydrin.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 317635; from *Chem. Zentr.*, 1920, ii, 445—446).—Hydrogen chloride is allowed to act on pinacone at a temperature which is above that at which the hydrogen chloride additive product is produced, and below that at which pinacolin is formed, or the additive product of pinacone and hydrogen chloride is heated to such a temperature. Pinacone chlorohydrin, a substance with a camphor-like odour, is formed quantitatively at 35—45°.

H. W.

**Preparation of Ethyl Ether.** ELEKTRIZITÄTSWERK LONZA (D.R.-P. 317589; from *Chem. Zentr.*, 1920, ii, 445).—Acetaldehyde vapour is treated with hydrogen in the absence of oxygen and presence of a contact agent.

In previous processes, alcohol has been invariably produced by passing mixtures of acetaldehyde and hydrogen over catalysts (compare this vol., i, 134); apparently, electrolytic hydrogen has been used, which invariably contains oxygen. Only traces of ether are formed from a gaseous mixture containing even a few tenths per cent. of oxygen, whilst, in the complete absence of the latter, mixtures of ether and alcohol are produced which contain up to 15% of the former. The production of ether commences at about 90°, whilst decomposition of the acetaldehyde begins at about 170°; the temperature of the reaction chamber must therefore be maintained between 90° and 170°. H. W.

**The Mechanism of the Reaction between Ethylene and Sulphur Chloride.** J. B. CONANT, E. B. HARTSHORN, and G. O. RICHARDSON (*J. Amer. Chem. Soc.*, 1920, **42**, 585—595).—The formation of  $\beta\beta'$ -dichlorodiethyl sulphide by the action of sulphur monochloride on ethylene at 40—60° is the result of two successive reactions, which take place with different velocities. Experiments with carbon tetrachloride and trichlorodiethyl sulphide having confirmed the proportionality of molecular concentration of solute to depression of freezing point of  $\beta\beta'$ -dichlorodiethyl sulphide, the relationship between ethylene absorption and dichlorodiethyl sulphide formation in the above reaction was determined by the addition of samples of the reaction mixture to such quantities of the pure sulphide as to depress its freezing point from 13.9° to 5—9°. Of the following pairs of figures, the first represents the percentage of sulphide in the reaction mixture when the ethylene absorbed was a percentage of the total eventually absorbed given by the second figure: 0.0, 23.8; 25.5, 45.0; 52.6, 67.25; 70.1, 87.5; 84.9, 100.0. The first stage in the reaction therefore consists in the formation of an intermediate compound, which only reacts further with ethylene when the absorption has reached about 30%; at the stage of 60—70% absorption, the reactions proceed at about the same rate, and later the second predominates completely. An intermediate compound from sulphur dichloride can be isolated in a fairly pure condition (with sulphur and chlorine contents 1% too low and too high, respectively, for the formula  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{SCI}$ ) by shaking it at 0° in excess of ethylene. The resulting pale yellow liquid apparently combines with sulphur when warmed with it, because the black, oily product is completely soluble in carbon tetrachloride, and is probably a polysulphide, since by oxidation with nitric acid, sulphuric acid and an unidentified organic sulphonic acid are produced. The intermediate product also evolves hydrogen chloride slowly at 0°, rapidly at 50°, very rapidly in presence of iron or ferric chloride at 5°, and is converted into a viscid, black oil. A similar product, which



behaves very similarly, is present in sulphur monochloride which has absorbed one mol. proportion of ethylene, but the presence of some unchanged monochloride and some dichlorodiethyl sulphide prevents its isolation. Although the ethylene absorbed by sulphur monochloride amounts to 95% of that theoretically required for its complete conversion into the sulphide, only about 80% of this is actually produced, whilst only about 50% of the calculated amount of sulphur is produced (it is not precipitated, but is in colloidal solution, from which it separates slowly at the ordinary temperature and rapidly at 100°, leaving the freezing point of the disulphide unchanged). Correspondingly, a black tar, completely soluble in organic solvents, and so free from elementary sulphur, remains when the sulphide is removed from the final product by distillation under reduced pressure. This tar corresponds approximately in composition with the formula  $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{S}_5$ , and, in conformity with this, by oxidation with nitric acid, gives sulphuric acid and a sulphonic acid, probably  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$  (compare Spring, A., 1888, 664). The tar is decomposed by steam at 200°, leaving a black residue rich in sulphur, whilst the steam removes a yellow oil, which boils under reduced pressure with decomposition, and is probably  $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{S}_3$ , since, on oxidation, it yields sulphuric acid and a sulphonic acid. That the tar is not a product of decomposition during distillation follows from the fact that its mixture with the requisite amount of pure dichlorodiethyl sulphide has the properties of the original crude product.

J. K.

**Chloromethyl Chloroformates.** ANDRÉ KLING, D. FLORENTIN, A. LASSIEUR, and R. SCHMUTZ (*Ann. Chim.*, 1920, [ix], 13, 44—59).—A more detailed account of work already published (compare this vol., i, 8, 139, 213).

W. G.

**Alcoholysis. II. Alcoholysis in the Absence of a Catalyst.** J. J. SUDBOROUGH, N. B. BHAGVAT, and V. K. BHAGVAT (*J. Ind. Inst. Sci.*, 1918, 2, 121—136).—A study of the alcoholysis in the absence of a catalyst of the methyl and ethyl esters of three pairs of acids, chosen so that each pair were similar in constitution, one being, however, a relatively strong acid and the other relatively weak. The results clearly indicate that esters derived from relatively strong acids enter into double decomposition with monohydric alcohols more readily than do the corresponding esters of weak acids.

Experiments made with methyl dichloroacetate and propyl alcohol confirmed these results, but in this case there was also a certain amount of replacement of the chlorine by the propyl group.

W. G.

**Colloid Chemical Studies of Soaps. III. Colloid Chemistry of Potassium Oleate and the Salting-out of Soaps. IV. Reaction of Soaps to Indicators.** M. H. FISCHER and MARION O. HOOKER (*Chem. Eng.*, 1919, 27, 253—257, 271—276. Compare this vol., i, 215).—In the first paper the various

theories are discussed that have been proposed to explain the salting out of soaps. The electrolytic theory which attributes the results to the neutralisation of the charge on the particles is inadequate. The authors advance the following. When small amounts of salt are added to a soap-water system the molecules of the former become hydrated and dispersed in the soap-water medium. Further addition of the salt causes not only a greater dehydration of the soap, but also an increase in the viscosity of the system due to the larger proportion of the disperse phase. When sufficient salt has been added the hydrated particles of salt touch one another and a reversal takes place, whereby the largely dehydrated soap becomes the disperse phase. As the density of the dehydrated soap is much less than that of the salt solution the former rises to the top.

In the second paper the contention is raised that a soap made from equivalent amounts of a fatty acid and a standard alkali solution is either acid, neutral, or alkaline toward an indicator, such as phenolphthalein, depending on the concentration of water in the system. A soap-water system may be water dispersed in hydrated soap or hydrated soap dispersed in water. Indicators react with the latter, but not with the former. On heating a soap gel the water may change from the disperse phase to the disperse medium. For this reason the indicator might react with the system at the higher temperature, where it could not do so with the cold gel. These facts must be borne in mind in the application of indicator methods to biochemistry. Living matter is made up of colloids containing water rather than of water containing colloids. It therefore is not always possible to determine by the use of an indicator whether living matter is acid, neutral, or basic. CHEMICAL ABSTRACTS.

**$\beta$ -Alkylthiolcrotonic Esters.** HELMUTH SCHEIBLER and JULIUS Voss (*Ber.*, 1920, **53**, [B], 379—388).—A series of  $\beta$ -alkylthiolcrotonic esters has been prepared by the action of sodium alkyl sulphides on the isomeric  $\beta$ -chlorocrotonic esters. In striking contrast to the behaviour of the corresponding free acids, it is found that the normal form is the more stable; isomerisation during the course of the reaction appears to depend not only on the mercaptan used, but also on the particular ester employed.

The  $\beta$ -chlorocrotonic esters are most advantageously prepared (yield, 90—95% of that theoretically possible) by converting the acids into their chlorides by means of thionyl chloride and treating the crude product of the reaction, after removal of excess of thionyl chloride, with the requisite alcohol.

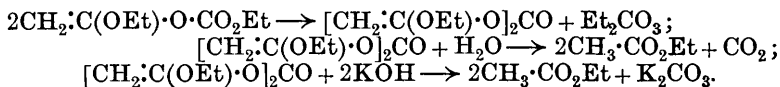
*Methyl  $\beta$ -benzylthiolcrotonate*, colourless, rhombic leaflets, m. p. 69—70°, is prepared by the action of a methyl-alcoholic solution of sodium benzyl sulphide on methyl chloroisocrotonate or methyl chlorocrotonate or from cold methyl alcohol and  $\beta$ -benzylthiolcrotonyl chloride. *Ethyl  $\beta$ -benzylthiolcrotonate*, six-sided plates or rhombic crystals, m. p. 64.5°, is exclusively formed by the action of ethyl  $\beta$ -chlorocrotonate on an alcoholic solution of sodium benzyl-

sulphide; with the corresponding *iso*-ester, however, the main product is *ethyl β-benzylthiolisocrotonate*, viscous, yellow oil, b. p. 204—205°/15 mm., but a small proportion is always converted into the normal ester. Ethyl *β-chloroisocrotonate* yields a mixture of the isomeric *ethyl β-ethylthiolcrotonates*; by fractionation of the product obtained by the action of sodium ethyl sulphide on the mixture of ethyl *β-chlorocrotonates* it was found possible to isolate the *iso*-ester, b. p. 125—126°/14 mm., 127—129°/16 mm., and 232—236°/ordinary pressure, and the normal ester, b. p. 139—141°/16 mm.

H. W.

**Metallic Compounds of the Enolic Forms of Carbonyl Compounds and their Application to Syntheses. I. Preparation and Properties of Metallic Compounds of Enolic Forms of Fatty Esters. Action of Ethyl Potassioacetate on Halogenacyl Compounds.** HELMUTH SCHEIBLER and JULIUS VOSS (*Ber.*, 1920, **53**, [B], 388—409. Compare Scheibler and Babe, A., 1916, i, 14).—The potassio-derivatives of esters which contain at least one hydrogen atom attached to the carbon atom in the  $\alpha$ -position to the carbalkyloxy-group are readily obtained when an ethereal solution of the ester is added to the finely-divided metal which is covered with ether heated to gentle ebullition; the metal dissolves immediately with evolution of hydrogen, and the metallic derivative remains more or less completely in colloidal solution in the ether. Sodium acts less energetically, and the corresponding derivatives can frequently be only obtained in boiling benzene or toluene solution, whereby they are partly decomposed. Increase in the weight of the alkyloxy-group appears to facilitate the reaction. The ester-enolates are very unstable substances, which, however, may be preserved for several days under ether in an atmosphere of hydrogen or nitrogen. Condensation with resulting formation of brown products occurs when their suspensions or solutions in benzene or toluene are warmed, and, on subsequent acidification with dilute mineral acids, acidic products are obtained. They are immediately decomposed by water into ester and alkali hydroxide; addition of alcohol causes the separation of alkyloxide. Dry oxygen is absorbed with formation of brown products. They react with carbon dioxide to give colourless potassium salts of carboxylic acids, which are stable towards oxygen and water, but contain the carboxyl group very loosely combined. They readily undergo addition, condensation, and substitution. Of the various derivatives prepared, ethyl potassio-acetate has been most fully investigated; apart from its mode of formation, the main evidence on which the formula,  $\text{CH}_2\text{:C(OK)·OEt}$ , proposed for it rests is its action toward ethyl chloroformate. When the substances are brought together in cold ethereal solution, potassium chloride is immediately precipitated, and the primary, unpleasant-smelling product is decomposed when the solution is boiled, yielding substances with an ester-like odour: on acidification of the solution, carbon dioxide, ethyl acetate, ethyl

carbonate, and ethyl malonate are obtained, the latter in very small amount. The reactions may be represented by the schemes:



The reaction just described offers a certain contrast to that observed by Bouveault and Locquin (A., 1906, i, 782), who, by the action of sodium on solutions of fatty esters in ether or benzene and decomposition of the products with water, obtained ketols; the difference is to be ascribed to the different mode of operation since, in the present instance, the experiments were performed in such a manner that the liberated hydrogen was immediately removed, whilst the French chemists worked at a lower temperature at which the reducing action of the gas could come into operation.

The following individual compounds are described: *ethyl potassioacetate*, pale yellow, amorphous, very hygroscopic powder; *methyl potassioacetate*, pale ochre-yellow; *ethyl sodioacetate*, pale reddish-yellow; *amyl sodioacetate*, yellow; *ethyl potassiopropionate*, pale yellowish-red; *ethyl potassiobutyrate*, yellow, amorphous powder; *ethyl potassiocrotonate*, ochre-coloured powder; *ethyl potassio- $\beta$ -ethoxycrotonate*; *methyl potassio- $\beta$ -ethylthiolcrotonate*, yellow powder, which does not absorb dry oxygen; *ethyl potassio- $\beta$ -ethylthiolcrotonate*, ochre-coloured powder; *ethyl potassio- $\beta$ -ethylthiolisocrotonate* resembles the preceding substance; *methyl sodio- $\beta$ -benzylthiolcrotonate*, red powder; *ethyl potassio- $\beta$ -benzylthiolcrotonate*, yellow; *ethyl sodio- $\beta$ -benzylthiolisocrotonate* resembles the isomeric compound; *ethyl dipotassio- $\beta\beta$ -thiodicrotonate*, wine-red powder; *ethyl potassiocinnamate*, red powder. Ethyl acetoacetate (1 mol.) and potassium (2 atoms) yield a white product which is readily soluble in ether to a brown solution, but half of the potassium remains unchanged. Ethyl  $\alpha$ -diethylacetoacetate evolves hydrogen when treated with potassium, and yields a yellowish-red, pulverulent, metallic derivative, which is probably formed by enolisation of the  $\beta$ -carbonyl group. Benzoic ester, on the other hand, does not evolve hydrogen when treated with potassium, but slowly gives a black product, which yields acidic substances after being decomposed by water.

The action of acetyl and benzoyl chlorides on ethyl potassioacetate is fundamentally similar to that of ethyl chloroformate. When the solutions are heated, however, various condensation products are formed. The primary product obtained by the use of acetyl chloride is smoothly converted by gaseous ammonia into acetamide and ethyl acetate,  $\text{NH}_3 + \text{CH}_2\text{:C(OEt)\cdot O\cdot COMe} = \text{CH}_3\text{:CO\cdot NH}_2 + \text{CH}_2\text{:C(OEt)\cdot OH} [\longrightarrow \text{CH}_3\text{:CO}_2\text{Et}]$ ; when, however, the product is distilled it gives alcohol, ethyl acetate, acetic acid, and acetic anhydride. Similarly, the substance formed when benzoyl chloride is employed yields alcohol, benzoic anhydride, ethyl benzoate, and benzoic acid. Alcohol and acid anhydride appear to be the primary decomposition products from which ester and acid are subsequently

formed. In addition, a highly unsaturated residue with a terpenaceous odour is obtained, which boils over a wide range of temperature and from which it has not been found possible to isolate any individual substance.

H. W.

**The Walden Inversion.** G. W. CLOUGH (*Helv. Chim. Acta*, 1920, **3**, 233—235).—The criticisms of Karrer and Kaase (A., 1919, i, 570) are based on a misconception of the author's views; further, the conclusions as to configuration drawn by Karrer and Kaase from their experimental observations on rotatory dispersion are premature in the present state of knowledge. The author doubts the wisdom of changing the designations of ordinary malic and aspartic acids from *l* to *d*.

J. K.

### **Preparation of Compounds of Deoxycholic Acid.**

HEINRICH WIELAND (D.R.-P. 317211; from *Chem. Zentr.*, 1920, ii, 447).—The acid is mixed with a hydrocarbon or other organic compound with the exception of ether and acetic acid.

Choleic acid from bile, which has hitherto been regarded as an isomeride of deoxycholic acid, is an additive product of the latter with fatty acids (palmitic, stearic, and oleic) in the proportion of eight molecules of deoxycholic acid to one molecule of fatty acid. The stable additive products (which are not dissociated in solution) of deoxycholic acid with hydrocarbons, alcohols, phenols, aldehydes, ketones, carboxylic acids, and their esters and alkaloids, which frequently contain the components in definite stoicheiometric relationship, are generally termed choleic acids, so, for example, camphorcholeic acid, phenolcholeic acid, etc. *Stearincholeic acid*, m. p. 186°, is prepared from deoxycholic acid and stearic acid dissolved in alcohol. *Naphthalenecholeic acid* [naphthalene (1 mol.) and deoxycholic acid (3 mols.)] has m. p. 182°. The choleic acids which are freely soluble in alcohol are prepared by dissolving deoxycholic acid in the molten component, allowing the product to crystallise, and removing the excess of the second component by a suitable solvent. *Phenolcholeic acid* crystallises from a small quantity of alcohol, is odourless, and yields sparingly soluble *calcium* and *barium* salts. *Benzaldehydecholeic acid*, from benzaldehyde (1 mol.) and deoxycholic acid (3 mols.), has m. p. 168°. The products are expected to find application in pharmacy.

H. W.

**The Enolisation of Carbonyl Compounds under the Influence of Grignard's Reagents.** VINAYAK KESHAV BHAGVAT and J. J. SUDBOROUGH (*J. Ind. Inst. Sci.*, 1919, **2**, 187—194).—Using the method described by Hibbert and Sudborough (T., 1904, **85**, 936) for the estimation of hydroxyl groups in carbon compounds by measuring the volume of methane produced by contact with an excess of magnesium methyl iodide solution, the authors have determined the enolisation produced in a number of aldehydes, ketones, and  $\beta$ -ketonic esters by contact with Grignard's reagents.

The results indicate that the carbonyl group in aldehydes and ketones is only enolised to a small extent, 11% being the maximum, under these conditions. In  $\beta$ -diketones and  $\beta$ -ketonic esters, how-

ever, the carbonyl group shows a very great tendency to undergo enolisation. In the case of benzoyl- and acetyl-acetone as much as 90% of the enolic form is produced. W. G.

**The Vapour Pressures of Acetone.** G. R. PARANJPÉ (*J. Ind. Inst. Sci.*, 1918, **2**, 47—58).—Using the statical method, the author has measured the vapour pressures of acetone over the temperature range  $-50^{\circ}$  to  $15^{\circ}$  for a sample of fermentation acetone,  $D_{25}^{25}$  0.7909, and for a sample of commercial "extra pure" acetone,  $D_{25}^{25}$  0.7865. W. G.

**Biochemical Synthesis of some Disaccharides: Glucobioses, Galactobioses.** ÉMILE BOURQUELOT (*Ann. Chim.*, 1920, [ix], **13**, 5—44).—A full account of work already published (compare A., 1913, i, 1080, 1305; 1914, i, 72, 499, 662; 1915, i, 76, 501, 940; 1916, i, 596; 1917, i, 250; 1919, i, 137, 361). W. G.

**Occurrence of Melezitose in Honey.** C. S. HUDSON and S. F. SHERWOOD (*J. Amer. Chem. Soc.*, 1920, **42**, 116—125).—The occurrence of melezitose in manna from the Douglas fir of British Columbia has recently been reported (A., 1919, i, 59); the same sugar has now been found in several samples of honey. In estimating the percentage of melezitose, advantage is taken of the fact that invertase hydrolyses sucrose, but not melezitose; the change in rotation after treatment with invertase and acid, respectively, is therefore determined, or, alternatively, the reducing power may be measured after similar treatment. H. W.

**Crystallography of Melezitose.** EDGAR T. WHERRY (*J. Amer. Chem. Soc.*, 1920, **42**, 125—128).—The crystals of melezitose dihydrate belong to the rhombic system, and are seemingly holohedral, but no doubt bisphenoidal,  $a:b:c=1.216:1.0496$ . Under the microscope, melezitose presents the form of plates and rods, in part rectangular in outline and in part terminated by faces inclined at large angles. The habit and the weak double refraction are useful in the identification of this sugar in honeys or honey dews; the dextrose which frequently separates from honeys is in rods terminated at one end by planes lying  $60^{\circ}$  apart, and rounded at the other end, and in parallel polarised light shows, at least in the centres of the grains, brilliant colours of the second order with — elongation. Sucrose can also be readily distinguished from melezitose by its much greater double refraction,  $\alpha$  being 1.45 and  $\gamma$  1.57, and by breaking into irregular fragments with oblique extinction. The refractive indices for melezitose for different wave-lengths are given in the appended table.

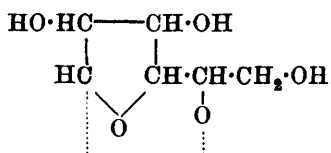
Index.	Wave-length.					
	450.	500.	550.	D 589.	600.	650.
$\alpha$ .....	1.550	1.546	1.542	1.540	1.540—	1.538
$\beta$ .....	1.558	1.553	1.550	1.548	1.547	1.545
$\gamma$ .....	1.561	1.556	1.552	1.550	1.549	1.547
$\gamma-\alpha$ .....	0.011	0.010	0.010	0.010	0.009+	0.009

H. W.

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### Glucosides. VI. Constitution and Configuration of Glucosides.

P. KARRER (*Helv. Chim. Acta*, 1920, 3, 258—260).—Pictet has been led by his observation that the lævogluco-  
 san obtained by distillation of starch and cellulose (A., 1918, i, 59)  
 can be similarly obtained from a number of glucosides (this vol.,  
 i, 66) to suggest that the  $\gamma$ -oxide formula for glucosides should  
 be modified. Since, however, he also found that ordinary  $\alpha$ -glucose  
 only yielded traces of the lævogluco-  
 san, and the glucosides he  
 examined were all  $\beta$ -compounds, it appeared to the author that  
 spatial configuration might be the determining factor in the reac-  
 tion. He confirmed this hypothesis



by showing that a considerable  
 amount of lævogluco-  
 san is obtainable  
 from  $\beta$ -glucose. Perhaps, therefore,  
 starch and cellulose contain  $\beta$ -gluco-  
 sidic linkings; it is possible that they  
 contain the lævogluco-  
 san grouping,  
 but not necessarily so. The struc-  
 ture of the trimethylglucose obtained from cellulose (Denham and  
 Woodhouse, T., 1917, 244) suggests that the glucose residues in  
 cellulose are coupled at the points indicated (see annexed  
 constitution).

J. K.

### The Substitution of Halogens for the Amino-group in Aliphatic Amines.

CHEMISCHE FABRIK FLORA (Brit. Pat. 132245).—The amino-groups of aliphatic amines may be replaced by  
 chlorine or bromine by treatment at 50—100° with a mixture of  
 nitric acid (D 1.4) and concentrated hydrochloric or hydrobromic  
 acid respectively. The reaction, which from the technical point  
 of view is particularly applicable to the amino-acids, such as leucine  
 or aspartic acid, is accompanied by vigorous evolution of nitrogen,  
 and proceeds without appreciable formation of by-products.  
 Instead of using a mixture of the two acids, nitric acid may be  
 used with a chloride or bromide, or the halogen acid with a nitrate.

G. F. M.

### Preparation, Crystallography, and Optical Properties of Methyl- and Ethyl-ammonium Mercuri-iodides.

GEORGE S. JAMIESON and EDGAR T. WHERRY (*J. Amer. Chem. Soc.*, 1920, 42, 136—145).—It has been found recently by Woodward and  
 Alsberg (unpublished work) that minute quantities of tertiary  
 methyl- and ethyl-amines can be precipitated and detected by  
 Mayer's reagent in the presence of primary and secondary amines  
 provided only small quantities of the latter are present; with  
 larger quantities, however, the latter substances also give pre-  
 cipitates, which are now described. All the substituted ammonium  
 mercuri-iodides are bright yellow in colour, and are decomposed  
 by water, with the separation of red mercuric iodide. They all  
 dissolve readily in an excess of potassium iodide, and care is there-

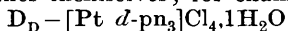
fore necessary in the preparation of Mayer's reagent, which is made by dissolving exactly 45 grams of mercuric iodide and 33 grams of potassium iodide so as to make 100 c.c. of solution.

*Dimethylammonium mercuri-iodide*,  $\text{NH}_2\text{Me}_2\text{HgI}_3$ , m. p.  $122^\circ$ , *trimethylammonium mercuri-iodide*, m. p.  $136^\circ$ , *diethylammonium mercuri-iodide*, m. p.  $114^\circ$ , and *triethylammonium mercuri-iodide*, m. p.  $77-78^\circ$  or  $59-60^\circ$ , according to the mode of preparation, are described. Dimethylamine and diethylamine cannot be detected in this manner if present in amounts less than 20 and 4 mg. per c.c. respectively.

The refractive indices of the compounds are extremely high (1.9 to 2.0), but cannot be accurately determined by the immersion method, since these substances are decomposed more or less rapidly by all suitable liquids. The following crystallographic data are recorded: *dimethylammonium mercuri-iodide*, monoclinic, domatic,  $a:b:c=0.9687:1:1.3406$ ,  $\beta=78^\circ 20'$ ; *diethylammonium mercuri-iodide*, rhombic, peri-cubic,  $a:b:c=1.1572:1:0.9102$ ; *trimethylammonium mercuri-iodide*, rhombic, peri-hexagonal,  $a:b:c=1.7262:1:0.9569$ ; *triethylammonium mercuri-iodide*, monoclinic, peri-tetragonal,  $a:b:c=1.15:1:1.08$ ,  $\beta=62^\circ 30'$ ; *tetramethylammonium mercuri-iodide*, rhombic, peri-hexagonal,  $a:b:c=0.59:1:0.52$ ; *tetraethylammonium mercuri-iodide*, tetragonal,  $a:c=1:1.1577$ .  
H. W.

### The Stereochemistry of the Platinum Atom; on Relatively Asymmetric Syntheses in Inorganic Complexes.

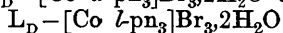
ALEXANDER P. SMIRNOV (*Helv. Chim. Acta*, 1920, 3, 177—195). —Werner has described the preparation and resolution into optically active components of the compounds  $[\text{Pt en}_3]\text{X}_4$  (*Vierteljahrsschrift Naturf. Ges. Zürich*, 1917, 62, 553), and the author now describes similar experiments with the salts  $[\text{Pt pn}_3]\text{X}_4$  (pn = propylenediamine). No isomerism conditioned by the *cis*- or *trans*-positions of the methyl groups was observed when either the racemic or one of the active forms of the diamine were used; all three series of salts closely resembled those derived from ethylenediamine, but their solubility, especially when the active forms were present, was much greater, and this at first prevented the resolution of the inactive forms. The molecular rotations of the salts derived from each of the active forms of diamine are remarkably high and of equal value, but of opposite sign, this being the same as those of the diamines themselves; for example,  $[\text{M}]_D$  for



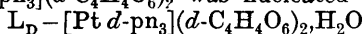
and for  $\text{L}_D - [\text{Pt } l\text{-pn}_3]\text{Cl}_4 \cdot 1\text{H}_2\text{O} = 1035^\circ$  and  $-1013^\circ$  respectively. It therefore seemed possible that the members of one series were the optical antipodes of those of the other, and this was confirmed by a consideration of the molecular rotations of the platinum compounds containing either one or two molecules of propylenediamine (Tschugaev and Sokolov, A., 1909, i, 137). From these it appears that the presence of each molecule of propylenediamine carries with it a rotation of  $96^\circ$ . In the above instances, the observed



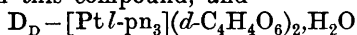
rotation is very much in excess of  $288^\circ$ , the value calculated on the basis of three molecules of diamine, and the difference represents the rotation due to the asymmetry of the complexes themselves. This difference, however, is considerably greater than that observed by Werner for the rotation of the optically active ethylenediamine salts, owing to the influence of the methyl groups. As the salts are colourless, they show no absorption in the visible spectrum or anomalous curve of rotatory dispersion, and no confirmation of the above conclusions is obtainable on optical grounds, but these are available in the case of the corresponding cobalt compounds. Thus, a comparison of the curves of molecular rotatory dispersion of  $D_D - [\text{Co } d\text{-pn}_3]\text{Br}_3 \cdot 2\text{H}_2\text{O}$  and



with those of  $d_D$  and  $l_D - [\text{Co en}_3]\text{Br}_3 \cdot 2\text{H}_2\text{O}$  shows that they have the same form, with points of inversion, respectively, at  $\mu\mu 503.5$  and  $492$ , and maxima (or minima, as the case may be) in the region  $\mu\mu 517-527$ . The values for the ethylenediamine salts are throughout numerically greater than those for the propylenediamine compounds, because these are composite values representing the effect of the active complexes and that of the active propylenediamine. The latter is always opposite in sign to the rotation of the free propylenediamine (Tschugaev and Sokolov), and, as a consequence, in the region where the values for the ethylenediamine derivatives show that the effect of the complex is scarcely perceptible, a second reversal of sign takes place at  $\mu\mu 626$ . Finally, the product which separated when a solution containing  $[\text{Pt } r\text{-pn}_3](d\text{-C}_4\text{H}_4\text{O}_6)_2$  was nucleated with



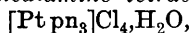
was identical with this compound, and



was obtained from the residual solution after treatment with potassium chloride.

In both cases, therefore, a total asymmetric synthesis has been effected, which is parallel to the formation of one rhamnohexonic acid and one mannoheptonic acid only from rhamnose and mannose (E. Fischer and others, A., 1888, 1049; 1889, 480). This phenomenon therefore extends to atoms with other spatial relationships than that of the tetrahedral carbon atom, and the internal spatial configuration of molecules associated with a central atom determines the spatial relationship of such molecules to that atom.

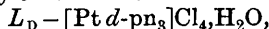
*r.-Platinum tripropylenediamine tetrachloride,*



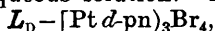
prepared by heating an alcoholic solution of chloroplatinic acid at  $100^\circ$  with *r.*-propylenediamine hydrochloride, forms a white, granular, crystalline powder after crystallisation from dilute alcohol; the *bromide*, *r.*- $[\text{Pt pn}_3]\text{Br}_4$ , from the chloride by double decomposition with sodium bromide, is a yellowish-white, crystalline powder; the *iodide*, *r.*- $[\text{Pt pn}_3]\text{I}_4$ , from the chloride and ammonium iodide, is orange-yellow, but blackens even in the dark;

the *sulphate*,  $r$ .-[Pt pn<sub>3</sub>](SO<sub>4</sub>)<sub>2</sub>, and the *nitrate*,  $r$ .-[Pt pn<sub>3</sub>](NO<sub>3</sub>)<sub>4</sub>, are obtained from the chloride and the corresponding silver salts.

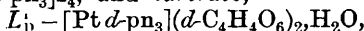
1-Platinum tripropylenediamine tetrachloride,



prepared from *d*-propylenediamine, has  $[M]_C - 844^\circ$ ,  $[M]_D - 1013^\circ$ ,  $[M]_E - 1419^\circ$  in 0.5% aqueous solution. The *bromide*,

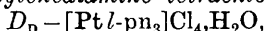


*iodide*,  $L_D - [Pt d\text{-}pn_3]I_4$ , and *tartrate*,



give very similar values for their molecular rotations.

*d*-Platinum tripropylenediamine tetrachloride,



has  $[M]_C + 839^\circ$ ,  $[M]_D + 1035^\circ$ ,  $[M]_E + 1413^\circ$  in 0.5% aqueous solution; the *bromide*,  $D_D - [Pt l\text{-}pn_3]Br_4$ , *iodide*,  $D_D - [Pt l\text{-}pn_3]I_4$ , and *tartrate*,  $D_D - [Pt l\text{-}pn_3](l\text{-}C_4H_4O_6)_2 \cdot H_2O$ , were also prepared.

The chloride and bromide of each of the last two series, obtained by resolution of the salts of the racemic series, agreed in their properties with the above description. From the chlorides, the respective active forms of propylenediamine were obtained by decomposition at 100° with formaldehyde solution.

Salts of the tri-*l*-propylenediaminecobalt-series have already been described (Tschugaev and Sokolov). Tri-*d*-propylenediaminecobalt bromide,  $D_D[Co d\text{-}pn_3]Br_3 \cdot 2H_2O$ , was prepared by heating *d*-propylenediamine with chloropentamminecobalt chloride, or 1:6-dichlorotetrapyridinecobalt chloride, or 1:6-dichlorodipropylenediaminecobalt chloride; the solution of the chloride thus obtained being treated with sodium bromide. Details are given of the values for the molecular rotations with various wave-lengths, from which the curves described above were constructed.

J. K.

**Preparation of Hexamethylenetetramine.** A. SANDER (*Zeitsch. angew. Chem.*, 1920, **33**, 84).—The author disputes Herzog's contention (this vol., i, 292) that the formation of hexamethylenetetramine by treatment in the cold of an ammonium salt with excess of formaldehyde is confined to the carbonate. The reaction also takes place with other ammonium salts, and may be utilised for their estimation. Ammonium carbonate, however, more readily yields a pure product than other salts. W. J. W.

**Synthesis of a Peptide of Aspartic Acid by means of Vegetable Enzymes.** C. RAVENNA (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 55—58).—Treatment of aqueous asparagine solution with pulped spinach leaves in presence of toluene for twenty days at about 25° appears to result in the formation of the dipeptide of aspartic acid, asparagylaspartic acid (compare this vol., i, 150, 151) in small proportion. Further experiments on a large scale are in progress. T. H. P.

**Compounds of Thiocyanates of certain Bivalent Metals and Hydrazine.** PRIYADARANJAN RÂY and PULIN VIHARI SARKAR (T., 1920, 117, 321—323).

**Chromic Thiocyanates.** NIELS BJERRUM (*Det. K. Danske. Vidensk. Selskabs Skrifter, Nat. Math.*, 1915, 7, pp. 66; from *Chem. Zentr.*, 1920, i, 414—415).—A full account is given of the complex chromic thiocyanates and their equilibrium.

Tervalent chromium yields the following complex ions with  $H_2O$  and CNS ( $CNS=X$ ), in which the water is replaced step by step by the CNS radicle:  $Cr aq_6^{+++}$ ,  $Cr aq_5 X^{++}$ ,  $Cr aq_4 X_2^+$ ,  $Cr aq_3 X_3$ ,  $Cr aq_2 X_4^-$ ,  $Cr aq X_5^{--}$ , and  $Cr X_6^{---}$ . The substance,  $Cr aq_3 X_3$ , is a non-electrolyte. The existence of the second and third complexes could be established in solution, but the corresponding substances could not be isolated in the solid state; they are insoluble in ether. *Trithiocyanotriquo-chromium* could be obtained in the crystalline condition, but not in a state of purity; in solution, it can be prepared in a much purer form. The molecular conductivity of a 0.1*N*-solution of the crystals is  $\mu=3.87$  at  $0^\circ$ , whilst, under similar conditions, the value  $\mu=250-300$  is in general observed for a tervalent electrolyte. When dried in a vacuum, the very hygroscopic crystals retain 3.2—3.6  $H_2O$ , which is obviously chemically combined in the complex. The *tetrathiocyano-complex* could be obtained in the form of a dilute solution of the free acid, from which the corresponding salts were prepared, but could not be isolated in the solid state. Quinine and strychnine yielded precipitates of varying composition; quinoline salts gave an oily precipitate. The free acid is freely soluble in ether, in which the salts do not dissolve. The *pentathiocyano-complex* was isolated as the beautifully crystalline *quinoline* salt, from which the free acid and the *sodium* salt were prepared. It contains 1  $H_2O$  in complex union; the free acid is soluble in ether, but the salts are not. The *quinoline* salt (which does not contain water of constitution) and the *pyridine* salt of the hexathiocyano-complex are described. All the chromothiocyano-complexes give reddish-violet solutions in water, the shade becoming more red and deeper with increasing CNS content.

For the soluble complexes the partition-coefficient between ether and water at the ordinary temperature is:  $Cr aq_3 X_3$ , ca. 3.6;  $H[Cr aq_2 X_4]$ , ca. 9.4;  $H_2[Cr aq X_5]$ , ca. 4;  $H_3[Cr X_6]$ , ca. 0.3. In the cases of the tri- and tetra-thiocyano-complexes the values for the partition-coefficient depend somewhat on the mode of preparation of the compounds, which probably points to the presence of mixtures of stereoisomerides, such as are to be expected from Werner's theory.

The velocity of decomposition of the several complexes has been measured by estimating the concentration of the CNS ions by the coloration with ferric nitrate. In aqueous solution, the stability of the hexathiocyano-complex is almost independent of the reaction of the solution. The remaining complexes become more stable in

acid solution as their CNS content diminishes, whilst the reverse is the case in alkaline solution. The trithiocyano-complex is fairly stable in ethereal solution, in which the stability of the other complexes rapidly diminishes with the CNS content. The complexes are sensitive to light.

Analytical methods for the estimation of the several complexes have been worked out. The hexa- and penta-complexes are first precipitated as quinoline salts, and their relative proportions in the precipitate are elucidated by estimation of the Cr and CNS content. The tri- and tetra-complexes are removed from the filtrate by means of ether when it is found possible to separate them by fractionation and to determine their amounts by two chromium estimations. Finally, chromium and thiocyanogen are titrimetrically estimated in the extracted aqueous solution, and the content of mono- and di-complex can then be calculated if the content of hexa-aquo-complex is known. The latter is determined by precipitation as chrome alum with potassium hydrogen sulphate and alcohol.

The chromothiocyano-complexes are slowly formed in solutions which contain the hexa-aquochrome-ion and the CNS ion. At the ordinary temperature, however, the stable state is not attained for some years. The chemical equilibrium between the various complexes and the CNS ion has been determined in aqueous solution at 50° for ten solutions. The results of chemical analysis are confirmed by measurements of the electrolytic conductivity. The affinity of the chromium atom for the CNS ion in normal solution is calculated from the equilibrium constants in the usual manner, and is found to be +3710 cal. for the first and -570 cal. for the last CNS group.

Graphs are given showing the relationship between the complexity and the concentration of the CNS ion, from which the equilibrium in a solution can be calculated if the concentrations of Cr and CNS are known.

H. W.

**The Thiocyanates of Gold and Free Thiocyanogen. Gold Chloride.** NIELS BJERRUM and AAGE KIRSCHNER (*Det. K. Danske Vidensk. Selskabs Skrifter, Nat. Math.*, 1918, **8**, pp. 76; from *Chem. Zentr.*, 1920, i, 415—417).—The thiocyanates of gold have been investigated, since they are representatives of very complex and somewhat unstable salts, and permit the examination of the different stages of oxidation of a metal. The behaviour of aurithiocyanates leads to the assumption of the existence of free thiocyanogen in solution.

Potassium aurithiocyanate,  $\text{KAuX}_4$  ( $\text{X} = \text{CNS}$ ), is very sparingly soluble in water, the solubility product being  $6 \times 10^{-5}$  in 1.4 ionic normal solution. Ammonium aurithiocyanate,  $\text{NH}_4\text{AuX}_4$ , is a reddish-yellow substance prepared by the precipitation of an aqueous solution of ammonium thiocyanate with a solution of auric chloride (0.4% Au) in hydrochloric acid. Sodium aurithiocyanate forms ruby-red needles, solubility product  $5 \times 10^{-4}$  in 2.2 ionic-normal solution. Hydrogen aurithiocyanate,  $\text{HAuX}_4 \cdot 2\text{H}_2\text{O}$ , forms dark red crystals and is prepared by mixing an acidified solution of

sodium thiocyanate with chloroauric acid and extracting the solution with ether. In pure solution, the aurithiocyanate is mainly present as the ion,  $\text{AuX}_4^-$ , the complexity constant of which,

$$K_X = \text{AuX}_4^- / \text{Au}^{+++} \times \text{X}^-,$$

is  $10^{17.7}$  times as great as that of the  $\text{AuCl}_4^-$  ion. It is dark reddish-brown in colour, and at  $\lambda = 578 \mu\mu$  has a molar extraction-coefficient, 108. When the concentration of the thiocyanate-ion is greater than 0.2, penta- and hexa-thiocyanoauri-ions are present in considerable amount, the complexity constants of which are  $K_{\text{AuX}_5} = \text{AuX}_5^- / \text{AuX}_4^- \times \text{X}^- = 1.0$  and  $K_{\text{AuX}_6} = \text{AuX}_6^{2-} / \text{AuX}_5^- \times \text{X}^- = 1.1$ . The colour is darker than that of the tetra-complex, whilst the molar extinction-coefficient for the penta-complex is about 218 and for the hexa-complex about 248 for  $\lambda = 578 \mu\mu$ . At low concentrations of the thiocyanogen and hydrogen ions, the tetra-complex appears to undergo hydrolysis according to the scheme  $\text{AuX}_4^- + \text{H}_2\text{O} = \text{AuX}_3(\text{OH})^- + \text{H}^+ + \text{X}^-$ , but even when  $\text{H}^+$  and  $\text{Rh}^- = 0.01$  scarcely more than 20% is thus decomposed. The tetra-thiocyanoauri-ion is dissociated into dithiocyanoauri-ion and free thiocyanogen,  $\text{AuX}_4^- = \text{AuX}_2^- + \text{X}_2$ , the latter functioning as a colourless, composite halogen, the activity of which lies between those of bromine and iodine; it is liberated from thiocyanates by bromine, but immediately displaces iodine from iodides. It is extremely unstable and rapidly undergoes hydrolysis in aqueous solution,  $3(\text{CNS})_2 + 4\text{H}_2\text{O} = 5\text{H}^+ + 5(\text{CNS})^- + \text{HCN} + \text{H}_2\text{SO}_4$ ; this final result is due to four partial processes: (1)  $(\text{CNS})_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{CNS}^- + \text{H}(\text{CNS})\text{O}$ ; (2)  $2\text{H}(\text{CNS})\text{O} \rightarrow \text{H}^+ + \text{CNS}^- + \text{H}(\text{CNS})\text{O}_2$ ; (3)  $\text{H}(\text{CNS})\text{O} + \text{H}(\text{CNS})\text{O}_2 \rightarrow \text{H}^+ + (\text{CNS})^- + \text{H}(\text{CNS})\text{O}_3$ ; (4)  $\text{H}(\text{CNS})\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{HCN} + \text{H}_2\text{SO}_4$ . The velocity of reaction is conditioned by the slow rate of the second process, for which the following equation is valid:  $d[\text{X}_2]/dt = -k'[\text{HXO}]^2 = -K\text{X}^2/[\text{H}^+]^2 \times [\text{X}^-]^2$ ,  $k$  being about 5 at  $18^\circ$ .

*Hydrogen aurothiocyanate*,  $\text{HAuX}_2$ , is prepared as an unstable oil by the reduction of hydrogen aurithiocyanate with sulphite, acidification of the solution, and extraction with ether. The corresponding *potassium* salt consists of slender, colourless needles readily soluble in alcohol, but decomposed by water. The *ammonium* salt is colourless and crystalline. The complexity constant of the  $\text{AuX}_2^-$  ion, which is present in the aqueous solution of these salts, is  $10^{22.4}$  times smaller than that of the corresponding cyanogen ion. *Mon-amminoaurorhithiocyanate*,  $\text{AuNH}_3\text{X}$ , from ammonia and dithiocyanoaurorhithiocyanate in reversible reaction, is unstable and sensitive to light.

Aurithiocyanate may be estimated in the presence of aurothiocyanate by titration with sulphite until a colourless solution results, since the latter ion is colourless. In solution, aurithiocyanate is converted into aurothiocyanate by auto-reduction in accordance with the scheme:  $3\text{AuX}_4^- + 4\text{H}_2\text{O} = 3\text{AuX}_2^- + 5\text{H}^+ + 5\text{X}^- + \text{HCN} + \text{H}_2\text{SO}_4$ ; the presence of hydrogen and thiocyanogen ions and of aurothiocyanate retards this action, which is caused by the instability of free thiocyanogen liberated owing to dissociation of

the aurithiocyanate. The rate of reaction can be calculated from the dissociation constant of aurithiocyanate and the velocity of decomposition of thiocyanogen. A solution of aurothiocyanate dissociates into gold and aurithiocyanate:  $3\text{AuX}_2^- = 2\text{Au} + \text{AuX}_4^- + 2\text{X}^-$ , the equilibrium constant of which is *ca.* 33. The rate of reciprocal action increases with decreasing concentration of H- and CNS-ions. The presence of gold powder catalyses the change. The conjoint effect of auto-reduction and precipitation of gold is that solutions of gold thiocyanate gradually deposit the whole of the metal.

In hydrochloric acid solution the gold of chloroauric acid is mainly present in the form of the ion,  $\text{AuCl}_4^-$ , which, in pure solution, is hydrolysed as follows:  $\text{AuCl}_4^- + \text{H}_2\text{O} = \text{AuCl}_3(\text{OH})^- + \text{H}^+ + \text{Cl}^-$ . The equilibrium constant is  $0.55 \times 10^{-4}$ .

The authors have estimated the following normal potentials at about  $18^\circ$  ( $\text{X} = \text{CNS}$ ): (1)  $\text{Au} + 2\text{X}^- = \text{AuX}_2^- + \ominus$ , 0.689 volt; (2)  $\text{AuX}_2^- + 2\text{Rh}^- = \text{AuX}_4^- + 2\ominus$ , 0.645 volt; (3)  $\text{Au} + 4\text{X}^- = \text{AuX}_4^- + 3\ominus$ , 0.660 volt; (4)  $\text{Au} + 4\text{Cl}^- = \text{AuCl}_4^- + 3\ominus$ , 1.001 volt; (5)  $2\text{X}^- = \text{X}_2 + 2\ominus$ , 0.769 volt. The value given by Abegg and Campbell for the normal potential of the gold auro-ion is untrustworthy, since when measurements of the gold electrode potential ion in concentrated nitric acid solution saturated with aurous oxide are made, it is, in reality, the oxidation potential of the nitric acid which is determined.

H. W.

### Isomerisation and Polymerisation of Methyl Thiocyanate.

J. GILLIS (*Rec. trav. Chim.*, 1920, **39**, 330—338. Compare A., 1918, i, 157).—By repeating Walden's work (compare A., 1906, ii, 336) it was found that, at  $130^\circ$ , the influence of different dissolved substances was variable. Except with cadmium iodide and sulphuric acid, the catalytic effect in causing isomerisation and polymerisation is a minimum. Methyl thiocyanate undergoes appreciable isomerisation at  $130^\circ$ , and polymerisation is also noticeable. The ebullioscopic constant of methylthiocarbimide is in agreement with the constant deduced from Trouton's law.

A study of the influence of temperature shows that isomerisation is practically a complete reaction, but it is always accompanied by some polymerisation. Foreign substances introduced into the methyl thiocyanate may have differing catalytic effects on the isomerisation and on the polymerisation. Thus cadmium iodide accelerates the former and sulphuric acid the latter.

W. G.

### New Method of Formation of Nitriles by Catalysis. A.

MAILHE (*Compt. rend.*, 1920, **170**, 813—815).—Aliphatic or aromatic nitriles may be prepared by passing the vapours of the corresponding esters, along with ammonia, over aluminium oxide or thorium oxide at  $500^\circ$  (compare A., 1918, i, 105). It is now shown that the ammonia may be replaced by the vapours of primary amines, the action being  $\text{R}\cdot\text{CO}_2\text{Et} + \text{C}_n\text{H}_{2n+1}\cdot\text{NH}_2 = \text{R}\cdot\text{CN} + \text{EtOH} + \text{H}_2\text{O} + \text{C}_n\text{H}_{2n}$ . In some cases, slight secondary actions occur.

W. G.

**Preparation of Unsaturated Nitriles by Catalysis.**

ALPHONSE MAILHE (*Bull. Soc. chim.*, 1920, [iv], **27**, 226—229).—The method of preparation of aliphatic or aromatic nitriles, by passing the vapours of the esters of the corresponding acids, along with ammonia, over aluminium oxide at 480—500° (compare preceding abstract), can be applied to the preparation of unsaturated nitriles, such as crotononitrile, oleonitrile, elaidonitrile, and cinnamonitrile.

W. G.

**An Isomeride of Potassium Ferricyanide. II. I. BELLUCCI**

(*Gazzetta*, 1920, **50**, i, 23—29).—Hauser and Biesalski's statement (*A.*, 1913, i, 26) that the green isomeride of potassium ferricyanide, described by Locke and Edwards (*A.*, 1899, i, 407, 557), and studied by Bellucci and Sabatini (*A.*, 1911, i, 430), Piutti (*A.*, 1912, ii, 712), and Wells (*A.*, 1913, i, 347), consists of the red ferricyanide contaminated with a trace of Prussian-blue, is denied.

T. H. P.

**Observations on some Organic Compounds of Arsenic.**

ALEX. MCKENZIE and JOHN KERFOOT WOOD (*T.*, 1920, **117**, 406—415).

**Influence of Position on the Boiling Points of Isomeric Benzene Derivatives.** NEVIL VINCENT SIDGWICK (*T.*, 1920, **117**, 389—395).

**Some Derivatives of *p*-Dichlorobenzene.**

JOYCE H. CROWELL and L. CHAS. RAIFORD (*J. Amer. Chem. Soc.*, 1920, **42**, 145—152).—The investigation was undertaken with the object of finding a method of utilising the considerable amounts of *p*-dichlorobenzene which are formed as by-products in the technical production of chlorobenzene.

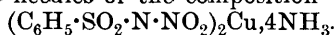
*p*-Dichlorobenzenesulphonic acid is most conveniently prepared (yield, 85—90%) by heating *p*-dichlorobenzene with sulphuric acid containing 10—12% of sulphur trioxide at 140—150°; 2:2':5:5'-tetrachlorodiphenylsulphone, colourless, diamond-shaped crystals, m. p. 179°, is also formed. 2:5-Dichloro-4-nitrobenzene cannot be conveniently sulphonated, since reaction does not occur below 150°, whilst, above this temperature, violent decomposition with almost complete decomposition occurs. 2:5-Dichloro-4-nitrobenzenesulphonic acid, flat, yellow, very hygroscopic needles, m. p. about 150°, can, however, be obtained by the action of fuming nitric acid (D 1.6) alone or in the presence of concentrated sulphuric acid on *p*-dichlorobenzenesulphonic acid (the sodium, potassium, ammonium, and barium salts are described). The constitution of the acid is deduced from the reduction of its sodium salt to the corresponding amino-compound (the acetyl derivative of which was prepared) and oxidation of the latter to 2:5-dichlorobenzoquinone. Reduction of an alkaline or faintly acid solution of the sodium salt of the nitrosulphonic acid yielded sodium 2:2':5:5'-tetrachloro-azobenzene-4:4'-disulphonate.

H. W.

**Benzenesulphonitroamide, Toluene-4-sulphonitroamide, 2-Nitrotoluene-4-sulphonitroamide and some of their Salts.**

BRUCE REID MATTHEWS (*J. Physical Chem.*, 1920, **24**, 108—119).

—A number of metallic salts of benzenesulphonitroamide, toluene-4-sulphonitroamide, and 2-nitrotoluene-4-sulphonitroamide have been prepared and described. *Ammonium benzenesulphonitroamide*,  $C_6H_5 \cdot SO_2 \cdot N(NO_2) \cdot NH_4$ , is formed by neutralising the free nitroamide with aqueous ammonia, and forms fine, yellow prisms; the corresponding *sodium*, colourless crystals; *calcium*, *barium*, *strontium*, *lithium*, *silver*, *copper*, and *nickel* salts are described, and also deep blue needles of the composition



*Strychnine benzenesulphonitroamide*,  $C_6H_5 \cdot SO_2 \cdot N_2O_2H, C_{21}H_{22}N_2O_9$ , is precipitated on adding strychnine nitrate to a hot aqueous solution of the ammonium salt.

Nitration of *p*-toluenesulphonamide with nitric acid (D 1.42—1.48) gives a mixture of *p*-toluenesulphonitroamide,  $C_6H_4Me \cdot SO_2 \cdot NH \cdot NO_2$ , and 2-nitrotoluene-4-sulphonitroamide, from which the former is extracted with ether; the residue obtained on evaporation of the ethereal solution, when recrystallised from toluene, gave a colourless, crystalline product, m. p. 110°. The *ammonium*, *potassium*, *barium*, *silver*, and *copper* salts are described. When silver oxide is added to an aqueous solution of the nitroamide, grey-coloured needles of the composition  $C_6H_4Me \cdot SO_2 \cdot NAg \cdot NO_2, 2NH_3$ , and a similar *copper* compound,  $(C_6H_4Me \cdot SO_2 \cdot N[NO_2])_2 Cu, 4NH_3$ , can be prepared. 2-Nitrotoluene-4-sulphonitroamide,  $NO_2 \cdot C_6H_3Me \cdot SO_2 \cdot NH \cdot NO_2$ , is obtained in the process described; nitric acid (D 1.48—1.50) being employed. It forms pale yellow needles, m. p. 118.5°. The *potassium*, *copper*, *silver*, *nickel*, and *manganese* salts are described, and also *silver* and *copper* salts containing  $2NH_3$  and  $5NH_3$  respectively. Practically all the salts described are very soluble in liquid ammonia.

J. F. S.

**Preparation of  $\alpha\beta$ -Dibromotetrahydronaphthalene and of  $\Delta^1$ -Dihydronaphthalene.** JULIUS VON BRAUN (D.R.-P., 316218; from *Chem. Zentr.*, 1920, ii, 241).—Tetrahydronaphthalene is treated with the calculated quantity of bromine at 100—140°, and the dibromotetrahydronaphthalene so produced is treated, if desired, with magnesium (1 atom) in the presence of ether or with tin (rather more than 1 atom) in the presence of alcohol.  $\alpha\beta$ -Dibromotetrahydronaphthalene has m. p. 69°;  $\Delta^1$ -dihydronaphthalene has b. p. 85°/15 mm., m. p. -8°,  $\alpha_D^{20}$  0.9963, and is quantitatively transformed by bromine into the dibromide.

H. W.

**Some Nitro-derivatives of Dimethylaniline.** J. SMIT (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 523—525).—In the nitration of 3:4-dinitrodimethylaniline, if the nitric acid contains much nitrous acid, or if the action proceeds for a long time, or if the temperature rises above 20°, nitroso-compounds are obtained



as well as 3:4:6- and 2:3:4-trinitrodimethylanilines. The author has isolated 3:4-dinitrophenylmethylnitrosoamine, m. p. 108—109°, and 3:4:6-trinitrophenylmethylnitrosoamine, m. p. 201°.

By the nitration of 3:6-dinitrodimethylaniline, in addition to the 3:4:6-trinitro-derivative, a small amount of 3:6-dinitrophenylmethylnitrosoamine, m. p. 132°, is obtained. In this nitration, the effect of nitrous acid on the reaction velocity is very great, and if the temperature of the reaction is perceptibly higher than the ordinary temperature, the only final product is 3:4:6-trinitrophenylmethylnitrosoamine.

W. G.

**Catalytic Decomposition of Schiff's Bases.** ALPHONSE MAILHE (*Bull. Soc. chim.*, 1920, [iv], 27, 229—234. Compare A., 1919, i, 395).—When Schiff's bases are passed alone over reduced nickel at 420—430°, a change first occurs which is similar to that which was found to occur during the catalytic hydrogenation (*loc. cit.*),  $RCH:NR' + 2H_2 = R\cdot CH_3 + R'NH_2$ , the hydrogen being formed by the partial destruction of the group  $R\cdot CH$ . In the second place, nitriles were formed, thus:  $RCH:NR' = RCN + R'H$ , this being, however, the less important change.

W. G.

**The Constitution of Capsaicin, the Pungent Principle of Capsicum.** II. E. K. NELSON (*J. Amer. Chem. Soc.*, 1920, 42, 597—599. Compare A., 1919, i, 543).—Octovanillylamide (this vol., i, 154), like capsaicin, is very stable towards alkalis, and is somewhat soluble in concentrated hydrochloric acid; also, free ammonia is easily liberated from free vanillylamine when it is boiled with water or solutions of alkaline carbonates, thus explaining its observation by Lapworth and Royle during the alkaline reduction of capsaicin (T., 1919, 115, 1109). The objections of these workers to the formulation of capsaicin as decenovanillylamide thus lose their force, and the author has now confirmed this formula by the regeneration of capsaicin from decenoyl chloride (obtained from the decenoic acid produced from capsaicin) and vanillylamine.

Indefinite results have been obtained from the oxidation of decenoic acid by chromic acid. By fusion with potassium hydroxide, acetic acid and an octoic acid, b. p. 240—245°, with a branched carbon chain, are produced. The silver octoate,  $C_8H_{15}O_2Ag$ , is sparingly soluble in water.

J. K.

**Influence of the Sulphonation of the Phenol on the Yields of Picric Acid.** M. MARQUEYROL and P. CARRÉ (*Bull. Soc. chim.*, 1920, [iv], 27, 195—199).—The yield of picric acid depends on the relative proportions of phenolsulphonic acid and phenoldisulphonic acid in the products of sulphonation of the phenol, the yields being much higher from the disulphonic acid. The maximum yield of phenoldisulphonic acid is obtained by carrying out the sulphonation for half an hour to one hour at 100° with five parts of 93% sulphuric acid to one part of phenol.

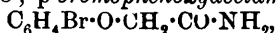
W. G.

**The Identification of Phenols. II.** JAMES A. LYMAN and E. EMMET REID (*J. Amer. Chem. Soc.*, 1920, **42**, 615—619. Compare A., 1917, i, 333).—*p*-Nitrobenzyl ethers have been prepared from a number of phenols. It is advisable to employ as solvents for the etherification of esters of salicylic acid the respective alcohols from which they are derived, and to avoid excess of alkali; otherwise interchange of the alkyl groups of the alcohol and of the ester takes place to a certain extent (compare Pardee and Reid, *J. Ind. Eng. Chem.*, 1920, **12**, 129). The *p*-nitrobenzyl ethers of the following phenols had the melting points indicated: *o*-nitrophenol, 130°; *p*-nitrophenol, 187·4°; 2:4-dinitrophenol, 248°; *o*-chlorophenol, 100°; *p*-chlorophenol, 101·3°; 2:4:6-tribromophenol, 163·5°; guaiacol, 63·6°;  $\alpha$ -naphthol, 140°;  $\beta$ -naphthol, 106·5°; salol, 87°; methyl salicylate, 128·2°; ethyl salicylate, 125°; butyl salicylate, 92°; *o*-tolyl salicylate, 142·5°; *m*-tolyl salicylate, 118°. J. K.

**A Comparison of the Activity of certain Unsaturated Groups with the Activity of the Allyl Group in certain Ethers.** S. G. POWELL and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1920, **42**, 646—658).—A comparison of various unsaturated ethers with phenyl allyl ethers in respect of the rearrangement of the latter into *o*-allylphenols. Of compounds containing, like the allyl derivatives, an unsaturated linking in the  $\beta\gamma$ -position to the oxygen atom, phenyl and *p*-bromophenyl propargyl ethers do not yield phenolic compounds when boiled, but suffer complete decomposition; phenoxyacetonitrile was decomposed to some extent when boiled, whilst a tarry product resulted from its *p*-methyl derivative, which, however, gave a little *p*-cresol when its solution in amyl ether was boiled; the chief products of decomposition of the benzyl ethers were not diphenylmethane, but benzene, derivatives, and their *p*-nitro- and *p*-bromo-derivatives suffered more or less profound decomposition. Contrary to the statement of D.R.-P. 268099, phenyl and *p*-tolyl vinyl ethers do not suffer rearrangement, but decompose when heated, yielding phenol and *p*-cresol.  $\delta$ -Phenoxy- $\Delta^{\alpha}$ -butene,  $\epsilon$ -phenoxy- $\Delta^{\beta}$ -pentene, and its  $\beta$ -methyl derivatives were all remarkably stable, and suffered neither rearrangement nor decomposition when boiled.

*Phenyl vinyl ether*,  $\text{CH}_2\text{:CH}\cdot\text{OPh}$ , from phenyl  $\beta$ -bromoethyl ether, b. p. 155—156°; *p*-tolyl vinyl ether,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{O}\cdot\text{CH}\text{:CH}_2$ , similarly prepared, with a pleasant odour, has b. p. 177—180°;  $n_{\text{D}}^{30}$  1·513;  $D_{25}^{30}$  0·975;  $\beta$ -*p*-bromophenoxyethyltrimethylammonium bromide,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_3\text{Br}$ , white crystals, from *p*-bromophenyl  $\beta$ -bromoethyl ether and trimethylamine.  $\gamma$ -Phenoxypropylmethylcarbinol,  $\text{OPh}\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{OH}$ , prepared by reduction of  $\gamma$ -phenoxypropyl methyl ketone, is a viscous oil, having b. p. 163°/20 mm.,  $n_{\text{D}}^{25}$  1·5123,  $D_{25}^{31}$  1·025; by treatment with phosphorus tribromide;  $\beta$ -bromo- $\epsilon$ -phenoxy-pentane,  $\text{OPh}\cdot[\text{CH}_2]_4\cdot\text{CHMeBr}$ , is obtained. It is an oil, b. p. 172°/28 mm., with  $n_{\text{D}}^{30}$  1·529,  $D_{25}^{32}$  1·258, and with alcoholic potash gives  $\epsilon$ -phenoxy- $\Delta^{\beta}$ -pentene.  $\epsilon$ -Phenoxy- $\beta$ -methyl- $\Delta^{\beta}$ -pentene,  $\text{OPh}\cdot[\text{CH}_2]_3\cdot\text{CH}\cdot\text{CMe}_2$ ,

b. p. 241°/745 mm.,  $n_D^{30}$  1.505, is prepared by fractionation of the product of the action of magnesium methyl iodide on ethyl  $\gamma$ -phenoxybutyrate. Phenyl  $\beta$ -bromoallyl ether,  $\text{OPh}\cdot\text{CH}_2\cdot\text{CBr}\cdot\text{CH}_2$ , for the preparation of phenyl propargyl ether, is best obtained from sodium phenoxide and tribromohydrin. Similarly, *p*-bromophenyl  $\beta$ -bromoallyl ether,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{OCH}_2\cdot\text{CBr}\cdot\text{CH}_2$ , is prepared from sodium *p*-bromophenoxide as an oil, b. p. 171°/22 mm.,  $n_D^{25}$  1.587,  $D_{25}^{25}$  1.719; *p*-bromophenyl propargyl ether,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{O}\cdot\text{CH}_2\cdot\text{C}\equiv\text{CH}$ , has b. p. 144°/24 mm.,  $n_D^{30}$  1.567, and  $D_{25}^{30}$  1.468; *p*-bromophenoxyacetamide,



forms needles, m. p. 148—149°; *p*-methoxyphenyl *p*-nitrobenzyl ether,  $\text{C}_{14}\text{H}_{13}\text{O}_4\text{N}$ , forms yellow needles, m. p. 88°; *p*-bromophenyl *p*-nitrobenzyl ether,  $\text{C}_{15}\text{H}_{10}\text{O}_3\text{NBr}$ , yellow needles, m. p. 112°; 2:4-dibromophenyl *p*-nitrobenzyl ether,  $\text{C}_{15}\text{H}_9\text{O}_3\text{NBr}_2$ , yellow needles, m. p. 161°.

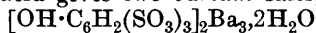
J. K.

### Preparation of Derivatives of *N*-Acylated-*p*-aminophenols.

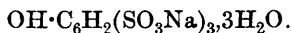
FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 316902; from *Chem. Zentr.*, 1920, ii, 374).—*N*-Acyl derivatives of *p*-aminophenols are caused to react with  $\alpha$ -bromo- $\alpha$ -ethylbutyrylcarbimide. Thus, the  $\alpha$ -bromo- $\alpha$ -ethylbutyrylurethane of *p*-acetylaminophenol,  $\text{CET}_2\text{Br}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$  (from bromoethylbutyrylcarbimide and a suspension of *p*-acetylaminophenol in acetone), forms small, colourless, shining leaflets, m. p. 144°. The  $\alpha$ -bromo- $\alpha$ -ethylbutyrylcarbamic ester of *p*-hydroxyphenylcarbamide, colourless crystals, has m. p. 187°. The products exhibit marked antipyretic and antineuralgic, and distinct sedative and hypnotic, action.

H. W.

**Phenoltrisulphonic Acid and its Transformation into Picric Acid.** M. MARQUEYROL and P. CARRÉ (*Bull. Soc. chim.*, 1920, [iv], 27, 199—204).—By the sulphonation of phenol with ten times its weight of sulphuric acid containing 20% of sulphur trioxide, a mixture of phenol-di- and -tri-sulphonic acids is obtained, which contains 80% of the trisulphonic acid. On nitration, the trisulphonic acid gives a yield of picric acid equivalent to 90% of theory. Thus, in the nitration of the phenolsulphonic acids, the yield of picric acid increases from the mono- up to the tri-sulphonic acid. The ionisation of these acids increases in the same order. Phenoltrisulphonic acid gives two barium salts,



and  $\text{C}_6\text{H}_2\cdot\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ (\text{SO}_3)_3 \end{array}\text{Ba}_2$ , and a sodium salt,



The barium salt is only very sparingly soluble in water, but barium sulphate may be washed free from it by 5% hydrochloric acid.

W. G.

**The Hydrolysis of Naphthyl Ethers.** GOPAL BALKRISHN KOLHATKAR (*J. Ind. Inst. Sci.*, 1919, 2, 179—186).— $\beta$ -Naphthyl

ethers are much more readily hydrolysed by hydrochloric acid than the corresponding  $\alpha$ -naphthyl ethers, whilst the corresponding phenyl ethers are only decomposed to a very slight extent under similar conditions.  $\beta$ -Naphthyl methyl ether is more readily hydrolysed than  $\beta$ -naphthyl ethyl ether. The amount of ether hydrolysed is practically independent of the amount of ether present, but is approximately proportional to the volume of acid present, and the time of the reaction, and is also influenced by the concentration of the acid.

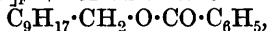
W. G.

**Preparation of Tetrahydro- $\beta$ -naphthyl Mercaptan.** GEORG SCHROETER and WALTHER SCHRAUTH (D.R.-P. 299604; from *Chem. Zentr.*, 1920, ii, 447).—Tetrahydronaphthalene is converted by chlorosulphonic acid into tetrahydronaphthalene- $\beta$ -sulphonyl chloride, which is then treated with reducing agents. The *sulphonyl chloride* has m. p. 55–56°, b. p. 194–195°/14 mm., and is converted by ammonia into *tetrahydronaphthalene- $\beta$ -sulphonamide*, m. p. 134–135°, and by potassium hydroxide solution (50%) into the crystalline potassium tetrahydronaphthalene- $\beta$ -sulphonate. The sulphonyl chloride is reduced by zinc dust and sulphuric or hydrochloric acid to *tetrahydro- $\beta$ -naphthylmercaptan*, b. p. 153–155°/26 mm., which has only a faint odour of mercaptan and yields a colourless, well-crystallised mercury salt. It is converted by methyl sulphate and alkali into the corresponding *methyl ether*, colourless, aromatic oil, b. p. 151°/14 mm. *Tetrahydronaphthylthiolacetic acid*,  $C_{10}H_{11} \cdot S \cdot CH_2 \cdot CO_2H$ , m. p. 133–135°, is formed by the action of chloroacetic acid on a solution of the thiol in sodium hydroxide, and subsequent addition of acid. An ammoniacal solution of the mercaptan is oxidised by air to *bistetrahydronaphthyl disulphide*,  $(C_{10}H_{11})_2S_2$ , m. p. 87–89°. The "thionaphthol" is designed for the preparation of drugs, disinfectants, dyes, and explosives.

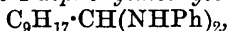
H. W.

**1:2:2:3-Tetramethylcyclopentane-1-carbinol and its Derivatives.** H. RUPE and P. LÄUGER (*Helv. Chim. Acta*, 1920, 3, 272–298).—The purposes of experimental stereochemistry demand a primary alcohol, of considerable optical activity, and easily convertible into stable esters, including those of the halogen acids. Myrtenol fulfils these requirements (A., 1915, ii, 717; Zäslin, *Diss.*, Basel, 1915), but is not easily accessible. Camphylcarbinol, otherwise suitable, is too readily dehydrated (A., 1919, i, 29). The authors have therefore studied anew the reduction of the carboxyl group of campholic acid by the method of Bouveault and Blanc, these workers having obtained very small yields in this case (A., 1904, i, 642). Apparently the first stage of such reductions consists in the addition of hydrogen with the formation of a hydro-derivative, because the yields in the present case gradually increase with the degree of unsaturation of the residue of the hydroxy-compound from which the ester is derived. Thus the ethyl, the *isobutyl*, the *isoamyl*, the  $\beta$ -naphthyl, and the phenyl esters respectively give yields of 10–15%, 22%, 25%, 64%, and 94–96%.

*β-Naphthyl campholate*,  $C_9H_{17} \cdot CO \cdot O \cdot C_{10}H_7$ , silky leaflets, m. p.  $70^\circ$ , is obtained from campholic chloride and either *β*-naphthol or its sodium salt. Phenyl campholate, prepared in a similar way, is a liquid, b. p.  $163^\circ/10$  mm. 1:2:2:3-Tetramethylcyclopentane-1-carbinol,  $C_9H_{17} \cdot CH_2 \cdot OH$ , prepared by reduction of phenyl campholate under carefully regulated conditions, for which the original should be consulted, is a waxy mass, m. p.  $64^\circ$ , b. p.  $96-96.5^\circ/10$  mm., with a disagreeably penetrating odour, reminiscent of that of fenchyl alcohol; in benzene, it has  $[\alpha]_D^{20} + 53.36^\circ$ ;  $[\alpha]_D^{20} + 67.18^\circ$ ;  $[\alpha]_{H_2}^{20} (\lambda = 546.3) + 79.42^\circ$ ;  $[\alpha]_F^{20} + 102.74^\circ$ . The benzoate,



is a viscid, colourless oil, almost odourless, b. p.  $186^\circ/12$  mm. The corresponding aldehyde may be obtained from the alcohol by direct oxidation, or by Bouveault's catalytic process with copper, but the yields are poor. Better results are obtained by Merling's process (A., 1908, i, 653), which involves the following series of reactions. Campholic chloride is converted into the anilide,  $C_9H_{17} \cdot CO \cdot NHPh$ , leaflets, m. p.  $93^\circ$ . The crude phenyliminochloride, obtained by treatment of the anilide with phosphorus pentachloride, reacts vigorously with aniline, with the production of the diphenyl amidine,  $C_9H_{17} \cdot C(:NPh) \cdot NHPh$ , leaflets, m. p.  $211^\circ$ ; this compound, by reduction in alcoholic solution with sodium, furnishes 1:2:2:3-tetramethylcyclopentane-1-diphenylmethylenediamine,



leaflets, m. p.  $76-77^\circ$ . This product, in its crude condition, after removal of impurities volatile in steam, is hydrolysed by the addition of sulphuric acid and continuing the steam distillation. The yield is 45–55%. 1:2:2:3-Tetramethylcyclopentane-1-aldehyde,  $C_9H_{17} \cdot CHO$ , m. p.  $37-38^\circ$ , b. p.  $73-74^\circ/8$  mm., resembles camphor in appearance, and has a somewhat disagreeable and penetrating odour. It has a burning taste. In alcoholic solution it slowly reduces Fehling's solution. In benzene,  $[\alpha]_D^{20} + 68.48^\circ$ ;  $[\alpha]_D^{20} + 89.26^\circ$ ;  $[\alpha]_{H_2}^{20} + 108.00^\circ$ ;  $[\alpha]_F^{20} + 148.65^\circ$ . It is characterised by its semicarbazone, fine needles, m. p.  $220-221^\circ$  (decomp.), its oxime, m. p.  $27-28^\circ$ , b. p.  $116.5-117^\circ/8$  mm., its phenylhydrazone, a yellow oil, b. p.  $189-190^\circ/8$  mm., easily decomposed even at ordinary temperatures; its p-nitrophenylhydrazone, yellow leaflets, m. p.  $145^\circ$ ; and its p-bromophenylhydrazone, red leaflets, m. p.  $145-146^\circ$ . Ethyl *β*-hydroxy-1:2:2:3-tetramethylcyclopentane-1-propionate,  $C_9H_{17} \cdot CH(OH) \cdot CH_2 \cdot CO_2Et$ , from the aldehyde, ethyl bromoacetate, and zinc, is a yellow oil, b. p.  $151-152^\circ/10$  mm. or  $264^\circ/730$  mm.; its acetyl derivative,  $C_9H_{17} \cdot CH(O \cdot Ac) \cdot CH_2 \cdot CO_2Et$ , is a colourless, viscid oil, b. p.  $165-167^\circ/13$  mm. *β*-Hydroxy-1:2:2:3-tetramethylcyclopentane-1-propionic acid,  $C_9H_{17} \cdot CH(OH) \cdot CH_2 \cdot CO_2H$ , prepared from the ester by hydrolysis with alcoholic potash, forms leaflets, m. p.  $79.5-80^\circ$  (decomp.  $140^\circ$ ), but can be distilled almost without decomposition at  $191-193^\circ/10$  mm. By dehydration with acetic anhydride it furnishes 1:2:2:3-tetramethylcyclopentane-1-acrylic acid,  $C_9H_{17} \cdot CH:CH \cdot CO_2H$ , long needles, m. p.  $101^\circ$ ; this compound may also be obtained by hydro-

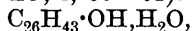
lysis of the above acetyl derivative, or by distilling under reduced pressure *ethyl β-bromo-1:2:2:3-tetramethylcyclopentane-1-propionate*,  $C_9H_{17}\cdot CHBr\cdot CH_2\cdot CO_2Et$ , a yellow oil, produced by the action of phosphorus tribromide on the hydroxy-ester. The acrylic acid is sparingly soluble in water, but readily in organic solvents; in benzene,  $[\alpha]_D^{20} + 52.06^\circ$ ;  $[\alpha]_D^{20} + 66.82^\circ$ ;  $[\alpha]_{H_2}^{20} + 79.90^\circ$ ;  $[\alpha]_F^{20} + 107.39^\circ$ . The *methyl ester*,  $C_{13}H_{22}O_2$ , is an oil, b. p.  $131-132^\circ/12$  mm.; the *chloride*,  $C_{12}H_{19}OCl$ , an oil, b. p.  $139^\circ/13$  mm.; the *ethyl ester*,  $C_{14}H_{24}O_2$ , an oil, b. p.  $149^\circ/12$  mm., has  $[\alpha]_D^{20} + 44.91^\circ$ ;  $[\alpha]_D^{20} + 57.51^\circ$ ,  $[\alpha]_{H_2}^{20} + 68.80^\circ$ ,  $[\alpha]_F^{20} + 91.93^\circ$ , and in benzene the values are  $+44.47^\circ$ ,  $57.11^\circ$ ,  $68.19^\circ$ , and  $91.60^\circ$ . 1:2:2:3-*Tetramethylcyclopentane-1-propionic acid*,  $C_9H_{17}\cdot CH_2\cdot CH_2\cdot CO_2H$ , is prepared by reduction of the acrylic acid in aqueous alcoholic solution in presence of a 40% nickel catalyst (A., 1919, i, 29); it crystallises in large, thin leaflets, m. p.  $89.5-90^\circ$ , and in benzene has  $[\alpha]_D^{20} + 38.21^\circ$ ,  $[\alpha]_D^{20} + 48.38^\circ$ ,  $[\alpha]_{H_2}^{20} + 57.20^\circ$ ,  $[\alpha]_F^{20} + 75.29^\circ$ ; the *magnesium salt*,  $[C_{12}H_{21}O_2]_2Mg$ , forms leaflets; the *chloride*,  $C_{12}H_{21}OCl$ , is an oil, b. p.  $129^\circ/12$  mm.; the *ethyl ester*,  $C_{14}H_{26}O_2$ , boils at  $138^\circ/12$  mm. and has  $[\alpha]_D^{20} + 32.32^\circ$ ;  $[\alpha]_D^{20} + 40.95^\circ$ ;  $[\alpha]_{H_2}^{20} + 48.59^\circ$ ;  $[\alpha]_F^{20} + 63.15^\circ$ , whilst in benzene the values are  $+32.94^\circ$ ,  $41.66^\circ$ ,  $49.14^\circ$ , and  $64.54^\circ$ . 1:2:2:3-*Tetramethylcyclopentylmethylcarbinol*,  $C_9H_{17}\cdot CHMe\cdot OH$ , from the above aldehyde and magnesium methyl iodide, is a clear liquid, b. p.  $96-98^\circ/11$  mm., with a faint odour of camphor; on oxidation it yields 1:2:2:3-tetramethylcyclopentyl methyl ketone, b. p.  $96-102^\circ/12$  mm. (Rupe and Kloppenburg, A., 1919, i, 539; Meerwein, A., 1919, i, 162). *Phenyl 1:2:2:3-tetramethylcyclopentylcarbinol*,  $C_9H_{17}\cdot CHPh\cdot OH$ , m. p.  $55^\circ$ , b. p.  $172-174^\circ/11$  mm., could not be oxidised to the ketone. 1:2:2:3-*Tetramethylcyclopentylstyrene*,  $C_9H_{17}\cdot CH\cdot CHPh$ , is obtained by boiling the crude condensation product from magnesium benzyl chloride and the above aldehyde with acetic anhydride, and forms leaflets with a blue fluorescence, m. p.  $51^\circ$ , b. p.  $146-149^\circ/11$  mm. 1:2:2:3-*Tetramethylcyclopentylbenzylcarbinyl acetate*,



needles, m. p.  $81-82^\circ$ , b. p.  $189-192^\circ/11$  mm., is also produced in the reaction.

J. K.

**Arbusterol and its Derivatives.** GIOVANNI SANI (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 59-61).—*Arbusterol*,



isolated from the oil of *Arbutus unedo* seeds, crystallises in aggregates of silky, white needles, resembling bits of straw, m. p.  $129^\circ$ ,  $[\alpha]_D^{15} - 15.33^\circ$ , its specific rotation being thus widely different from those of other phytosterols. In chloroform solution it gives with sulphuric acid a cherry-red coloration, changing to dirty violet with a purple reflexion, whilst the acid becomes at first yellow and later brown, with a green fluorescence. Its *benzoyl* derivative,  $C_{26}H_{43}\cdot OBz$ , forms shining, elongated, rectangular scales, m. p.  $137^\circ$ , and its *acetyl* derivative,  $C_{26}H_{43}\cdot OAc$ , crystals, m. p.  $110^\circ$ . The pro-

portions of halogens fixed by arbusterol differ from those fixed by other cholesterol, and are being further investigated. T. H. P.

### Volatility in Steam: Benzoic Acid and its Derivatives.

NEVIL VINCENT SIDGWICK (T., 1920, 117, 396—406).

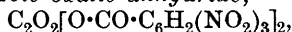
### The Use of Oxalyl Chloride and Bromide for Producing Acid Chlorides, Acid Bromides, or Acid Anhydrides. III.

ROGER ADAMS and L. H. Ulich (*J. Amer. Chem. Soc.*, 1920, 42, 599—611).—When the method of preparation of aromatic anhydrides from 1 mol. of oxalyl chloride and 2 mols. of acid (A., 1918, i, 165) is applied to *m*- or *p*-nitro-, 3:5-dinitro-, or 2:4:6-trinitro-benzoic acid, mixed anhydrides, very stable towards excess of chloride, are obtained, and these, except in the case of the last compound, when melted give the simple anhydrides. Probably, therefore, in general the course of the reaction is expressed as follows:  $2\text{RCO}_2\text{H} + (\text{COCl})_2 \rightarrow 2\text{HCl} + (\text{R}\cdot\text{CO}_2\cdot\text{CO})_2 \rightarrow (\text{R}\cdot\text{CO})_2\text{O} + \text{CO}_2$ . Less favourable results are obtained with aliphatic acids than with aromatic compounds, some acid being unchanged, and some acid chloride being produced. Acid chlorides may be prepared smoothly and in good yield by boiling acid anhydrides, including those of the nitro-compounds above, with 1.5—2.5 mols. of oxalyl chloride alone or in presence of benzene for two hours; the anhydrides may be replaced by aromatic or aliphatic acids themselves, but in this case the nitrobenzoic acids only give the mixed anhydrides. Arsenic trichloride and chromyl chloride were also successfully prepared from their oxides by this method. Either anhydrides or chlorides are, however, better prepared from the sodium salts of the acids and 1 or 1—1.5 mols. respectively of oxalyl chloride in benzene solution. Possibly, in this case, mixed anhydrides are not intermediate products, because the nitrobenzoic acids do not exhibit the exceptional behaviour previously noted. Oxalyl bromide behaves in a similar manner to the chloride; better yields of acid bromides were obtained than with phosphorus pentabromide.

Excellent yields of benzanilide, anisanilide, and *p*-toluanilide were obtained from ethereal solutions of the appropriate ketoximes on adding 0.75 mol. oxalyl chloride, which therefore promotes the Beckmann rearrangement very effectively.

*p*-Nitrobenzoic oxalic anhydride,  $\text{C}_2\text{O}_2(\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ , yellow crystals, which melt and decompose at 169—170°.

2:4:6-Trinitrobenzoic oxalic anhydride,



yellow crystals, melts and decomposes at 228—230°, but, unlike the other anhydrides of this type, furnishes 1:3:5-trinitrobenzene, and with sodium carbonate solution easily gives sodium trinitrobenzoate.

*o*-Chlorobenzoyl bromide,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{COBr}$ , has b. p. 143—145°/37 mm.; *m*-chlorobenzoyl bromide, b. p. 143—147°/40 mm.; *p*-chlorobenzoyl bromide, b. p. 141—143°/27 mm.; *o*-bromobenzoyl bromide, b. p. 166—168°/18 mm.; *p*-bromobenzoyl bromide, b. p. 135—137°/18 mm.; *p*-iodobenzoyl bromide, m. p. 54—55°, rapidly

darkens; *o*-toluoyl bromide, b. p. 133—136°/37 mm.; *m*-toluoyl bromide, b. p. 136—137°/52 mm.; *p*-toluoyl bromide, b. p. 145—149°/42 mm.; *p*-methoxybenzoyl bromide, b. p. 183—186°/27 mm.; *m*-nitrobenzoyl bromide, m. p. 42—43°, b. p. 165—167°/18 mm.; *p*-nitrobenzoyl bromide, m. p. 63—64°, b. p. 165—167°/18 mm.; *cinnamyl bromide*, m. p. 47—48°, b. p. 180—184°/40 mm.; *phenylacetyl bromide*, b. p. 150—155°/50 mm.  
J. K.

**Alcoholysis. III. The Alcoholysis of Aromatic Esters and the Inhibiting Influence of Ortho-substituents.** J. J. SUDBOROUGH and D. D. KARVÉ (*J. Ind. Inst. Sci.*, 1919, **3**, 1—14. Compare this vol., i, 364).—The results obtained with a large number of esters of aromatic acids indicate quite clearly that sodium alkyl oxides or hydrochloric acid are excellent catalysts for the alcoholysis of these esters. An ethyl ester may readily be converted into the corresponding methyl ester by dissolving it in ten times its weight of methyl alcohol, adding a small piece of sodium, and warming for ten minutes. Two substituents in ortho-positions to the ester group completely inhibit the change. The following new esters have been prepared and characterised.

*Ethyl 3:5-dibromobenzoate*, m. p. 51°, is obtained by eliminating the amino-group from *ethyl 3:5-dibromo-4-aminobenzoate*, m. p. 108°, which is prepared by brominating ethyl *p*-aminobenzoate in dilute sulphuric acid solution. *Methyl 3:5-dibromo-4-aminobenzoate* has m. p. 127—128°; *ethyl 2:4:6-tribromobenzoate*, m. p. 80°. *Ethyl 2:4:6-tribromo-3-aminobenzoate*, m. p. 61—62°, was prepared from the silver salt of the acid and ethyl iodide. *Methyl 2:4:6-tribromo-3-aminobenzoate* has m. p. 96—97°. *Ethyl 2:3:4:6-tetrabromobenzoate* has m. p. 31°; *isobutyl p*-nitrobenzoate has m. p. 64—65°; *propyl 3:5-dinitrobenzoate* has m. p. 71°; *isobutyl 3:5-dinitrobenzoate* has m. p. 85°; *ethyl 2:6-dinitrobenzoate* has m. p. 75·5°.

W. G.

**Preparation of *p*-Carbamidophenylacetylcarbamide and Related Compounds.** MARY RISING (*J. Amer. Chem. Soc.*, 1920, **42**, 128—136. Compare Rising and Stieglitz, *A.*, 1918, i, 271).—The successful preparation of *p*-carbamidophenylacetylcarbamide is described as the first of a series of carbamidophenylacetylcarbamides which are intended to form a basis for the study of their physiological activity, particularly as hypnotics.

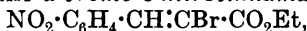
*p*-Nitrophenylacetyl chloride is condensed with carbamide in boiling benzene to yield *p*-nitrophenylacetylcarbamide, m. p. 237—239°, after preliminary softening and depending on the rate of heating (Jacobs and Heidelberger, *A.*, 1918, i, 90, give m. p. 250—252°). This substance is quantitatively reduced by a solution of stannous chloride in cold glacial acetic acid which has been saturated with hydrogen chloride to *p*-aminophenylacetylcarbamide, which decomposes without melting at 192—193°, and, in the form of its *hydrochloride*, is converted by potassium cyanate into *p*-carbamidophenylacetylcarbamide,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ .



The preparation of the following related carbamide derivatives is also described: methyl *p*-aminophenylacetate, b. p. 140—150°/17 mm., and its hydrochloride from *p*-aminophenylacetonitrile; *p*-carbamidophenylacetonitrile, m. p. 170·5°, from potassium cyanate and *p*-aminophenylacetonitrile hydrochloride; methyl *p*-carbamidophenylacetate, colourless, shining needles, m. p. 131—132°, by the esterification of *p*-carbamidophenylacetonitrile and from methyl *p*-aminophenylacetate hydrochloride and potassium cyanate; *p*-carbamidophenylacetic acid, m. p. 184—185° (decomp.), by hydrolysis of the corresponding methyl ester.

The ethylation of phenylacetonitrile with metallic sodium or sodamide and ethyl iodide is fully discussed. H. W.

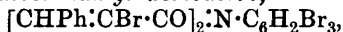
**$\alpha$ -Bromo-*o*- and -*p*-nitrocinnamic Acids.** S. REICH and N. Y. CHANG (*Helv. Chim. Acta*, 1920, **3**, 235—240).—A mixture of the two stereoisomeric ethyl  $\alpha$ -bromo-*p*-nitrocinnamates is produced in quantitative yield when an alcoholic solution of equimolecular proportions of ethyl  $\alpha\beta$ -dibromo- $\beta$ -*p*-nitrophenylpropionate and anhydrous sodium acetate is boiled for two hours. The esters may be separated mechanically after crystallisation from light petroleum, and undergo hydrolysis to the respective acids by treatment at 100° with a mixture of glacial acetic acid (five parts), sulphuric acid (one part), and water (one part). *allo*- $\alpha$ -Bromo-*p*-nitrocinnamic acid, like its meta-isomeride (Reich and others, A., 1918, i, 262), does not undergo condensation into a dibromodinitrotruxone when treated with sulphuric acid; it is unchanged by the cold acid, whilst at 100° it is converted into its stable isomeride. *Ethyl allo- $\alpha$ -bromo-*o*-nitrocinnamate*,



is a yellow oil, which does not solidify, and results as the sole product of the action of sodium acetate on ethyl  $\alpha\beta$ -dibromo- $\beta$ -*o*-nitrophenylpropionate. By hydrolysis under the above conditions, it is converted into the stable form of the corresponding acid (Naar, A., 1882, 840), the stability of the *allo*-forms of the three *allo- $\alpha$* -bromonitrocinnamic acids and their esters increasing in the order *ortho*-, *meta*-, *para*-.  $\alpha\beta$ -Dibromo- $\beta$ -*p*-nitrophenylpropionic acid furnishes a *bromo-*p*-nitrostyrene*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CHBr}$ , pale yellow needles, m. p. 45—46°, by treatment with sodium acetate in absolute alcoholic solution; if aqueous sodium acetate or sodium carbonate be used, a *stereoisomeride*, pale yellow needles, m. p. 123°, is obtained. The same tribromo-compound, m. p. 83°, is produced from each by the action of bromine. *Bromo-*o*-nitrostyrene*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CHBr}$ , is similarly obtained in two forms, yellow, m. p. 70°, and a yellow oil, which each furnish a tribromo-compound, m. p. 80°. J. K.

**Influence of the Weight of Radicles on the Isomerisation of Ethylenic Compounds.** S. REICH and RENÉE COUCHET (*Helv. Chim. Acta*, 1920, **3**, 240—243).—*allo- $\alpha$ -Bromocinnamtribromo-*

*anilide*,  $C_{15}H_9ONBr_4$ , m. p.  $193^\circ$ , accompanied by a small quantity of the *diallo- $\alpha$ -bromocinnamyl derivative*,



m. p.  $150^\circ$ , was prepared from the acid by treatment successively with phosphorus pentachloride in ethereal solution and tribromoaniline in benzene solution. By exposure in benzene solution to light for sixty hours, or in presence of bromine in chloroform solution, it is changed into the stable *isomeride*, needles, m. p.  $150^\circ$ . This compound was also prepared in a similar manner from its acid, the treatment with phosphorus pentachloride being carried out in boiling toluene solution. *allo- $\alpha$ -Bromocinnamic anhydride* (Michael and Bucher, A., 1898, i, 256) is produced by the action of acetic anhydride on the acid. It is isomerised by exposure to light for two weeks, but not by bromine. The latter result is possibly due to failure of the bromine to attach itself to the double bond rather than to the weight of the radicle. Stable  *$\alpha$ -bromocinnamic anhydride*,  $C_{18}H_{18}O_3Br_2$ , prepared in a similar manner, forms needles, m. p.  $100^\circ$ . J. K.

**The Truxillic Acids.** A. W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 509—511).—The truxillic acids may best be separated from cinnamic acid by sublimation in a current of air at  $130^\circ$ . The truxillic acids may be separated from one another by the following process. The mixture of acids is dissolved in the calculated quantity of *N*/10-potassium hydroxide, and to the solution 1.5 grams of anhydrous calcium chloride are added for each 10 c.c. After twenty-four hours, the precipitated calcium salts of  $\beta$ -,  $\delta$ -, and  $\epsilon$ -truxillic acids are filtered off. The other acids are separated from the filtrate by hydrochloric acid and ether, and the process as above is repeated. To the final filtrate 8.5 grams of calcium chloride are added for each 10 c.c., the calcium salt of  $\beta$ -cocaic acid being precipitated and filtered off. From the filtrate,  $\alpha$ - and  $\gamma$ -truxillic acids are separated by hydrochloric acid and ether, and the  $\gamma$ -acid is finally separated from the  $\alpha$ -acid by its solubility in hot water. The mixture of calcium salts of  $\beta$ -,  $\delta$ -, and  $\epsilon$ -truxillic acids, obtained as above, is converted into the barium salts, which are separated by their varying solubility in water.

$\beta$ -Cocaic acid gives with cinnamic acid a crystalline double acid, m. p.  $139^\circ$ . The ammonium salts of the truxillic acids slowly lose their ammonia when their aqueous solutions are evaporated on a water-bath, and are transformed into the free acids. W. G.

### Action of Cyanogen Bromide on Hydrocarbons and Phenol Ethers under the Influence of Aluminium Chloride.

P. KARRER, A. REBMANN, and E. ZEILER (*Helv. Chim. Acta*, 1920, **3**, 261—272).—A study of the range of applicability of the process for the synthesis of nitriles recently described (A., 1919, i, 591). Excellent yields were obtained of 3-cyanoacenaphthene and 2-cyanothiophen (owing to the agreement in properties between

the 2- and the 3-isomerides, the constitution given in the latter case is only presumed); less satisfactory results are obtained with *m*-methyl-*tert*.-butylbenzene, which gives a mixture, probably of 4- and 6-cyano-derivatives, and naphthalene, which also gives a mixture. Acenaphthylene, indene, and diphenyl were unchanged. The phenol ethers give even better results than the hydrocarbons; 2:4-dimethoxy-, 2:5-dimethoxy-, 3:4-dimethoxy-, and 2:3:4-trimethoxy-benzonitriles, 4-ethoxy- and 2-methoxy-naphthonitriles, were satisfactorily obtained from the corresponding ethers, being usually accompanied by small amounts of hydroxy-nitriles, due to hydrolysis of the alkyloxy-groups by aluminium chloride. Diphenyl and anthranol methyl ethers were recovered unchanged. Cyanogen chloride gives the same products as the bromide, and is almost equally reactive. Cyanogen iodide, however, is less useful, since it suffers decomposition to a considerable extent. The use of cyanogen bromide which has been kept for some time leads, in the case of benzene, to the formation of cyaphenin. As this was the sole product obtained by Scholl and Nörr in their original study of the reaction (A., 1900, i, 386), it would appear that they used polymerised material.

4-Ethoxynaphthonitrile,  $\text{OEt} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CN}$ , m. p.  $85^\circ$ , is hydrolysed by alcoholic potash to the corresponding acid; 2-methoxynaphthonitrile,  $\text{OMe} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CN}$ , m. p.  $94^\circ$ , however, only yields the 2-methoxynaphthamide,  $\text{OMe} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CO} \cdot \text{NH}_2$ , m. p.  $150^\circ$ . 2:3:4-Trimethoxybenzonitrile,  $\text{C}_6\text{H}_2(\text{OMe})_3 \cdot \text{CN}$ , fine needles, m. p.  $58^\circ$ , 1:3-dimethoxybenzonitrile,  $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CN}$ , m. p.  $89^\circ$ , and 2-hydroxy-4-methoxybenzonitrile,  $\text{OH} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{CN}$ , m. p.  $151^\circ$ , furnish the corresponding acids. A monomethyl ether of 2:5-dihydroxybenzonitrile,  $\text{OH} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{CN}$ , has m. p.  $122^\circ$ .

J. K.

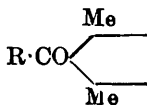
**Synthesis of Monobasic Acids by the Action of Malonic Acid on the Substituted Benzhydrols. Replacement of the Hydroxyl by the Group  $\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .** R. FOSSE (*Ann. Chim.*, 1920, [ix], 13, 105—120).—A full account of work already published (compare A., 1907, i, 136). W. G.

**The Constitution of the Dimethylcyclohexanone obtained by Methylation of the Sodium Derivative of  $\alpha$ -Methylcyclohexanone.** A. HALLER and R. CORNUBERT (*Compt. rend.*, 1920, 170, 700—705).—A further study of the dimethyl derivative obtained by the action of methyl iodide on  $\alpha$ -methylcyclohexanone in the presence of sodamide (compare Haller, A., 1913, i, 984). Benzaldehyde condenses with this dimethylcyclohexanone in the presence of sodium ethoxide to give a benzylidene derivative, m. p.  $82$ — $82.5^\circ$  (compare Auwers and Krollpfeiffer, A., 1915, i, 818). If the condensation occurs in the presence of dry hydrogen chloride, several products are obtained, of which the principal one is the benzylidene derivative mentioned above. In addition, the authors have isolated an isomeric substance, a yellow liquid, b. p.  $197$ — $198^\circ/28$  mm. (corr.), and two isomeric, crystal-

line compounds,  $C_{22}H_{24}O_2$ , one having m. p. 117—118°, and the other m. p. 188—190°, which are apparently products of the abnormal condensation of one molecule of dimethylcyclohexanone with two molecules of benzaldehyde. The authors agree with Auwers and Krollpfeiffer (*loc. cit.*) that the dimethylcyclohexanone under examination is a 1:1-dimethyl-2-compound.

W. G.

**Condensation of Acetophenone by means of Sodium Ethoxide.** II. C. CASTALDI (*Gazzetta*, 1920, 50, i, 71—81. Compare A., 1916, i, 31).—The author has investigated further the compound, m. p. 182°, obtained as one of the products of the condensation of acetophenone with sodium ethoxide (*loc. cit.*). This compound is probably identical with the one, m. p. 183°, obtained by Stobbe (A., 1901, i, 549) by condensing acetophenone with ethyl malonate by means of dry sodium ethoxide in presence of anhydrous ether; this author attributed to it the formula  $C_{24}H_{18}O$ , and, on the basis of its failure to react with phenylhydrazine or hydroxylamine, considered that the oxygen atom is not present as carbonyl. By the work of Feith and Davies (A., 1892, 314), Hantzsch (A., 1891, 35), and Baum (A., 1896, i, 222), it has, however, been shown that the carboxylic oxygen of the group (annexed formula) reacts with phenylhydrazine or hydroxylamine only when R is a carboxyl group, and not when it is either methoxyl or phenyl.



Gentle oxidation of the compound with nitric acid yields either 6-benzoyl-3:5-diphenylbenzoic acid or 4-benzoyl-3:5-diphenylbenzoic acid, the sodium salt of which yields 1:3-diphenylbenzene, carbon dioxide, and benzene (?) when dry-distilled. The compound must, therefore, be regarded as either 6-benzoyl-3:5-diphenyltoluene or 4-benzoyl-3:5-diphenyltoluene, and confirmation of this structure is afforded by the fact that it is obtainable also by the action of benzoyl chloride on 3:5-diphenyltoluene in carbon disulphide solution and in presence of aluminium chloride.

6-Benzoyl-3:5-diphenyltoluene or 4-benzoyl-3:5-diphenyltoluene,  $C_{26}H_{20}O$ , forms shining laminæ, m. p. 186° (not 182° as previously stated), has the normal molecular weight in freezing benzene, and dissolves in cold concentrated sulphuric acid, giving an intense violet-red solution.

6-Benzoyl-3:5-diphenylbenzoic acid or 4-benzoyl-3:5-diphenylbenzoic acid,  $C_{26}H_{18}O_3$ , forms faintly yellow, prismatic needles, m. p. 240° (decomp.), and dissolves in the cold in concentrated sulphuric acid, giving an intense violet coloration. The sodium salt (+4H<sub>2</sub>O) was prepared.

Diphenylbenzyltoluene,  $C_6H_2MePh_2 \cdot CH_2Ph$ , obtained by reducing the benzoyldiphenyltoluene by means of red phosphorus and hydriodic acid, crystallises in colourless needles, m. p. 125°, and gives no coloration with concentrated sulphuric acid.

T. H. P.

**Reduction and Fission of Halogenated Ketones by Tertiary Bases.** KARL VON AUWERS and ELISABETH LÄMMERHIET (*Ber.*, 1920, 53, [B], 428—443).—The conversion of *m*- $\alpha$ -bromoisobutyryl-*p*-cresol into 3:6-dimethylchromanone by the action of boiling dimethyl- or diethyl-aniline (A., 1914, i, 1136) does not appear to be an instance of a general reaction, since the examination of a series of  $\alpha$ -halogenated acyl-*p*-cresols shows that, as a rule, the parent halogen-free compound is regenerated, whilst chromanones or coumaranones are only formed in relatively small amount. The detection of coumaranones in the presence of keto-phenols is best effected with the aid of *p*-nitrophenylhydrazine, which converts the former into the sparingly soluble dinitro-osazones of the corresponding diketones, and the latter into the more readily soluble nitrophenylhydrazones. The same reagent may be used to distinguish between coumaranones and chromanones, since the latter, like the monocyclic ketones, only yield readily soluble mono-derivatives. The separation of keto-phenols and chromanones is not smoothly effected by treatment with alkali hydroxides, and is best accomplished by protracted warming of the mixture with semicarbazide. Mixtures of free keto-phenols and their ethers, such as are frequently obtained by the condensation of phenol ethers with acid chlorides in the Friedel-Craft's reaction, are not readily separated by means of alkali hydroxide and ether; removal of the phenols is, however, effected by shaking the solution of the mixed substances in light petroleum with aqueous methyl-alcoholic potassium hydroxide solution (compare Claisen, A., 1919, i, 266).

*o*-Chloroacetyl-*p*-cresol, when boiled with diethylaniline, is mainly converted into 4-methylcoumaranone (identified as the dinitro-osazone of *p*-tolylglyoxal, m. p. 260—265° [subsequent communication]), small amounts of acetyl-*p*-cresol (*p*-nitrophenylhydrazone, orange-red, shining needles, m. p. 245—246°) being also formed. Under similar conditions, *o*- $\alpha$ -chloropropionyl-*p*-cresol gives *o*-propionyl-*p*-cresol (*p*-nitrophenylhydrazone, m. p. 185—186°) and a little 1:4-dimethylcoumaranone. *o*- $\alpha$ -Bromo-*n*-butyryl-*p*-cresol yields *o*-butyryl-*p*-cresol, coarse, shining prisms, m. p. 33—34° (*semicarbazone*, long needles, m. p. 188—189°), and 2:6-dimethylchromanone. *o*- $\alpha$ -Chloroisovaleryl-*p*-cresol is smoothly reduced by dimethyl- or diethyl-aniline to *o*-isovaleryl-*p*-cresol (*p*-nitrophenylhydrazone, orange-red, silky needles, m. p. 136—137°; *semicarbazone*, coarse needles or prisms, m. p. 203—204°, when rapidly heated). The identity of the ketone is established by its synthesis from isovaleryl chloride and *p*-tolyl methyl ether; it has b. p. 151°/21 mm.,  $D_4^{18.4}$  1.0291,  $D_4^{20}$  1.028,  $n_D^{18.4}$  1.52683,  $n_D^{18.4}$  1.53270,  $n_D^{18.4}$  1.55001,  $n_D^{18.4}$  1.56848,  $n_D^{20}$  1.5320.  $\alpha$ -Bromo-*n*-butyrophenone, colourless, mobile oil, b. p. 145—147°/14 mm.,  $D_4^{13.25}$  1.3724,  $D_4^{20}$  1.364,  $n_D^{13.25}$  1.55996,  $n_D^{13.25}$  1.56520,  $n_D^{13.25}$  1.58035,  $n_D^{13.25}$  1.59378,  $n_D^{20}$  1.5622, is prepared from  $\alpha$ -bromo-*n*-butyryl bromide, benzene, and aluminium chloride, and is converted by diethylaniline into butyrophenone, pale yellow oil, b. p. 120—125°/21 mm. (*p*-nitrophenylhydrazone, orange-red needles,

m. p. 161.5—162.5°).  $\alpha$ -Bromoisobutyrophenone is a pale yellow oil, b. p. 135—137°/17 mm.,  $D_4^{14}$  1.3613,  $D_4^{20}$  1.355,  $n_D^{14}$  1.55425,  $n_D^{14}$  1.55923,  $n_D^{14}$  1.57369,  $n_D^{14}$  1.58617,  $n_D^{20}$  1.5567, which is transformed by diethylaniline into a mixture of approximately equal quantities of isopropyl- and isopropenyl-phenyl ketones.  $\alpha$ -Bromoisobutyryl bromide reacts with *m*-5-xylenol methyl ether in the presence of aluminium chloride to yield 1:1:3:5-tetramethylcoumaranone and 2-isobutyryl-*m*-5-xyleneol, m. p. 93—94°, the partial reduction of the brominated ketone primarily formed being effected by the liberated hydrogen bromide.

The conversion of  $\alpha$ -bromoisobutyryl-*p*-cresol into *p*-cresotic acid by boiling pyridine has been previously described (Auwers, *loc. cit.*); the same acid is similarly obtained from the  $\alpha$ -chloro-derivatives of *o*-propionyl-, *o*-butyryl-, and *o*-isovaleryl-*p*-cresol. Hydroxyl-free, halogenated ketones behave in the same manner; thus, benzoic acid is obtained from  $\alpha$ -bromo-*n*-butyro- and  $\alpha$ -bromoisobutyro-phenones. It appears possible that the first step in the action consists in the withdrawal of halogen acid from the compound, with the formation of a substance with an unsaturated side-chain; *p*-tolyl isobutenyl ketone is, however, unaffected by protracted boiling with pyridine. The action of quinoline differs from that of pyridine, since, for example, cresotic acid is not produced when it reacts with  $\alpha$ -chloroisovaleryl-*p*-cresol; small quantities of 2:2:6-trimethylchromanone can, however, be isolated.

H. W.

**The Reduction of Aromatic Ketones.** W. D. COHEN (*Rec. trav. chim.*, 1920, **39**, 243—279).—It has previously been shown (A., 1919, i, 124, 210) that in acid solution, benzophenone is reduced, with the formation of benzopinacol, whilst in alkaline medium, benzhydrol is the product. When the reducing agent is aluminium amalgam, a mixture of the two is obtained, the amount of benzhydrol depending on the rate at which the pinacol is attacked, owing to the slightly alkaline reaction set up at the moment of reduction. It is now shown that in an absolutely neutral medium, the benzophenone being reduced in absolute alcohol by means of light, benzopinacol is the only product. The velocity of formation of benzopinacol under these conditions is proportional to the concentration of the alcohol and the amount of active light, but is independent of the concentration of the ketone. The thermal coefficient of this photochemical reaction is small, being about 1.1 for 10°. The velocity of the reaction depends to some extent on the character of the alcohol, but the nature of the ketone is the principal factor in directing the reaction. Substituted ketones are attacked less quickly than benzophenone itself. The relationships observed between the different ketones are independent of the alcohol used. This photochemical reduction of aromatic ketones by alcohols in sunlight is an irreversible reaction.

The actinic light is situated in the violet part of the visible spectrum, and probably in the neighbourhood of the rays 404.7 and 407.8  $\mu$ . The absorption of the ketones is selective. In a mixture of two ketones, one of them may absorb a part of the light necessary for the reduction of the other, and there may thus be a disturbance in the relative rates of reduction. W. G.

**Action of an Alcoholic Solution of Potassium Hydroxide on Ketones. V. *p*-Hydroxybenzophenones.** P. J. MONTAGNE (*Rec. trav. chim.*, 1920, **39**, 339—349. Compare A., 1917, i, 143).—4-Hydroxybenzophenone does not undergo any reduction when boiled with alcoholic potassium hydroxide even for six days, and the introduction of a chlorine or bromine atom into the para-position in the other nucleus has no influence.

4-Ethoxybenzophenone is slowly converted, under the same conditions, into 4-ethoxybenzhydrol, and the action is accelerated by the introduction of a chlorine or bromine atom into the para-position in the other nucleus. In this case, at the same time, a secondary reaction occurs, the chlorine or bromine becoming replaced by an ethoxy-group, giving 4:4'-diethoxybenzophenone.

The following new compounds are described: 4-chloro-4'-ethoxybenzophenone, m. p. 121.25° (corr.), b. p. 223°/12 mm.; 4-chloro-4'-ethoxybenzhydrol, m. p. 69.5° (corr.); 4:4'-diethoxybenzophenone, m. p. 131.5° (corr.), b. p. 248°/15 mm.; 4-bromo-4'-ethoxybenzhydrol, m. p. 80.5°. W. G.

**Action of an Alcoholic Solution of Potassium Hydroxide on Ketones. VI. Iodobenzophenones.** P. J. MONTAGNE (*Rec. trav. chim.*, 1920, **39**, 350—357. Compare preceding abstract).—Both 2-iodo- and 4-iodo-benzophenone are completely transformed into benzhydrol, the iodine being removed, when boiled with alcoholic potassium hydroxide. Under the same conditions, 3-iodobenzophenone is only partly converted into benzhydrol, part of it remaining unchanged. If an ethoxy-group is introduced into the iodobenzophenone, as in 4-iodo-4'-ethoxybenzophenone, the iodine is removed by boiling with alcoholic potassium hydroxide, but in this case the ethoxy-group exerts its influence in preventing the reduction, and the product is ethoxybenzophenone.

Chloro- and bromo-benzhydrols do not lose their halogen when boiled with alcoholic potassium hydroxide, but under similar conditions 4-iodobenzhydrol and, to a lesser extent, 3-iodobenzhydrol have their iodine removed.

*m*-Iodobenzoyl chloride condenses with benzene in sunlight in the presence of aluminium chloride to give 3-iodobenzophenone, m. p. 42.5°, b. p. 226°/18 mm. It yields 3-iodobenzhydrol, m. p. 54°. 4-Iodo-4'-ethoxybenzophenone, m. p. 147.5°, b. p. 266°/17 mm., prepared from *p*-iodobenzoyl chloride and phenetole, gives 4-iodobenzhydrol, m. p. 73°. W. G.

**The Resin from Species of Xanthorrhoea not previously examined.** EDWARD HENRY RENNIE, WILLIAM TERNENT COOKE, and HEDLEY HERBERT FINLAYSON (T., 1920, 117, 338—350).

**Glucosides. V. Synthesis of  $\beta$ -Gaultherin, of Methyl  $\beta$ -Tetra-acetylglucosidoanthranilate, and of  $\beta$ -Glucosido-resorcylic Acid Methyl Ether.** P. KARRER and H. WEIDMANN (*Helv. Chim. Acta*, 1920, 3, 252—257. Compare A., 1919, i, 594).—The action of diazomethane on an ice-cold alcoholic solution of glucosidosalicylic acid results in the formation of the *methyl ester*,  $C_{14}H_{18}O_8$ , associated with 1 mol. of alcohol of crystallisation, as leaflets, m. p. 90—92°,  $[\alpha]_D^{15} - 53.78^\circ$  in alcohol. It is freed from alcohol by heating in a vacuum at 70°, and then has m. p. 105°. It gives no colour with ferric chloride and, whilst structurally identical with natural gaultherin, differs from it in that it is hydrolysed by emulsin, but not by gaultherase. Gaultherin is therefore the  $\alpha$ -stereoisomeride. The *tetra-acetyl* derivative of the above ester,  $C_{22}H_{26}O_{12}$ , needles, m. p. 154°,  $[\alpha]_D^{13} - 44.77^\circ$  in chloroform, is identical with Mauthner's product (A., 1918, i, 544), which therefore is not tetra-acetyl gaultherin. *Methyl  $\beta$ -tetra-acetylglucosidoanthranilate*,  $C_{22}H_{27}O_{11}N$ , prepared from the acid by treatment with diazomethane, forms needles, m. p. 165°,  $[\alpha]_D - 54.88^\circ$  in chloroform.  *$\beta$ -Tetra-acetyl glucosido-4-methoxysalicylic acid*,

$C_{22}H_{26}O_{13}$ , m. p. 160°,  $[\alpha]_D^{15} - 48.81^\circ$  in alcohol, is obtained by condensation of silver 4-methoxysalicylate with acetobromoglucose. It gives no colour with ferric chloride. By hydrolysis with cold baryta it yields  *$\beta$ -d-glucosido-4-methoxysalicylic acid*, needles, m. p. 163°,  $[\alpha]_D^{15} - 81.55^\circ$  in water. It is hydrolysed by emulsin, and gives no colour with ferric chloride. The *tetra-acetylglucose ester* of 4-methoxysalicylic acid,  $C_{22}H_{26}O_{13}$ , is also produced in the above condensation. It forms needles, m. p. 147°,  $[\alpha]_D^{16} - 45.37^\circ$  in chloroform. J. K.

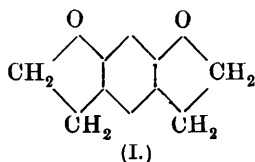
### Syntheses of Chromans [Benzopyrans] and Coumarans.

**II.** R. E. RINDFUSZ, P. M. GINNINGS, and V. L. HARNACK (*J. Amer. Chem. Soc.*, 1920, 42, 157—165).—The methods described previously (A., 1919, i, 342) have been applied to substituted phenols. In general, it is found that the dehydration of hydroxyethyl and hydroxypropyl phenyl ethers can be effected more conveniently with phosphoric oxide than with zinc chloride. The procedure consists in boiling the mixture of reagents for about an hour in the presence of an inert solvent (such as toluene or methyl ethyl ketone), the boiling point of which is such as to allow a fairly high temperature being attained without, however, rendering the subsequent fractionation of the product a matter of difficulty.

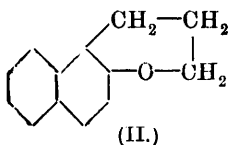
The following compounds are described: *o-tolyl  $\gamma$ -hydroxypropyl ether*, b. p. 174—176°/42 mm.,  $D_{20}^{29} 1.053$ ,  $n_D^{20} 1.523$ ; *o-tolyl  $\gamma$ -bromopropyl ether*, b. p. 154—156°/20 mm.,  $D_{20}^{29} 1.299$ ,  $n_D^{20} 1.535$ ; *8-methylbenzopyran*, b. p. 114—116°/20 mm.,  $D_{20}^{29} 1.039$ ,  $n_D^{20} 1.542$ ; *o-tolyl  $\beta$ -hydroxyethyl ether*, b. p. 143—145°/20 mm.,  $D_{20}^{29} 1.079$ ,  $n_D^{20} 1.528$ ;



*o*-tolyl  $\beta$ -bromoethyl ether, b. p. 133—134°/20 mm.,  $D_{20}^{29}$  1.360,  $n_D^{20}$  1.544; 6-methylcoumaran, b. p. 119—120°/65 mm.,  $D_{20}^{29}$  1.060,



$n_D^{27}$  1.527; *p*-bromophenyl  $\gamma$ -hydroxypropyl ether, b. p. 206°/48 mm.,  $D_{24}^{24}$  1.442,  $n_D^{22}$  1.563; 6-bromobenzopyran, b. p. 143—144°/18 mm.,  $D_{25}^{25}$  1.465,  $n_D^{22}$  1.580; *p*-bromophenyl  $\beta$ -bromoethyl ether, b. p. 165°/16 mm., m. p. 56°; 4-bromocoumaran, b. p. 135°/20 mm.,  $D_{20}^{20}$  1.436,  $n_D^{22}$  1.555; *p*-bromophenyl  $\beta$ -hydroxyethyl ether, b. p. 184°/20 mm., m. p. 49—50°; *m*-phenylene di- $\beta$ -hydroxyethyl ether,  $C_6H_4(O\cdot CH_2\cdot CH_2\cdot OH)_2$ , b. p. 230—234°/30 mm., m. p. 81°; *s*-benzotetrahydrodipyrane (formula I), b. p. 110—113°/148 mm.,  $D_{25}^{25}$  0.861,  $n_D^{22}$  1.448; *m*-phenylene di-



$\gamma$ -hydroxypropyl ether, b. p. 246—248°/20 mm.,  $D_{31}^{31}$  1.145,  $n_D^{21}$  1.529; *s*-benzotetrahydrodipyrane, b. p. 97°/75 mm.,  $n_D^{21}$  1.448;  $\beta$ -naphthyl  $\gamma$ -hydroxypropyl ether, m. p. 99—99.5°;  $\beta$ -naphthadihydropyran (formula II), m. p. 41—42°;  $\beta$ -naphthyl  $\beta$ -hydroxyethyl ether, m. p. 76—77°;  $\beta$ -naphthadihydrofuran, b. p. 185°/10 mm. (some decomp.),  $D_{30}^{30}$  1.0066,  $n_D^{23}$  1.482;  $\beta$ -naphthyl  $\beta$ -bromoethyl ether, m. p. 91.5—92.5°. H. W.

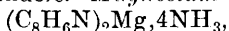
**Synthesis of Acids by the Action of Acid Anhydrides on Alcohols containing a Pyran Ring. Replacement of the Hydroxyl by the Group  $\cdot CH_2\cdot CO_2H$  or the Group  $\cdot CHR\cdot CO_2H$ .** R. FOSSE (*Ann. Chim.*, 1920, [ix], **13**, 87—104).—A full account of work already published (compare A., 1906, i, 691). W. G.

**Constitution of Ephedrine. Deoxyephedrine.** A. OGATA (*J. Pharm. Soc. Japan*, 1919, **451**, 751—764).—By a comparison of the physical constants of the two bases and of their salts, the author shows that deoxyephedrine is identical with *d*- $\beta$ -phenylisopropylmethylamine, prepared by reducing with sodium and alcohol the condensation product obtained by keeping a mixture of benzyl methyl ketone and alcoholic methylamine for four weeks, and resolving the racemic base obtained with tartaric acid. Consequently, ephedrine has the constitution  $OH\cdot CHPh\cdot CHMe\cdot NHMe$ .

CHEMICAL ABSTRACTS.

**Metallic Salts of Pyrrole, Indole, and Carbazole.** EDWARD C. FRANKLIN (*J. Physical Chem.*, 1920, **24**, 81—99).—The "ammono-acids" (compare A., 1905, i, 582; 1912, ii, 437), pyrrole, indole, and carbazole, have been converted into their metallic salts by the action of metals (sodium, potassium, magnesium, or calcium) or the metal amides (sodium, potassium, silver) on solution of the "ammono-acids" in liquid ammonia. In the case of pyrrole, a crystalline potassium salt could not be obtained, and on evaporating the solution an amorphous, viscous mass was always produced. Sodium forms a crystalline compound with pyrrole,  $C_4H_4NNa\cdot NH_3$ , on cooling the solution to the temperature produced by solid carbon dioxide and ether. This compound loses ammonia at 20° and yields the compound,  $C_4H_4NNa$ ; it is hydrolysed by water, yielding pyrrole

and sodium hydroxide. *Calcium pyrrole*,  $(C_4H_4N)_2Ca, 4NH_3$ , forms colourless crystals, but on losing its ammonia to form the "anammonous" salt it becomes slightly yellow, and has the dull appearance of an effloresced salt. It is vigorously attacked by water and pyrrole and calcium hydroxide are formed. In the preparation from metallic calcium it is shown that there is a deficiency in the hydrogen evolved which is due to the formation of a small amount of tetrahydropyrrole. *Magnesium pyrrole*,  $(C_4H_4N)_2Mg, 2NH_3$ , forms colourless crystals. *Silver pyrrole*,  $C_4H_4NAg, NH_3$ , is a well-crystallised product, which on keeping rapidly turns grey, and finally becomes black. The sodium and potassium salts of indole both form amorphous, viscous masses, from which it was not possible to obtain crystals. *Calcium indole*,  $(C_8H_6N)_2Ca, 4NH_3$ , forms beautiful, white crystals, which on heating to  $100^\circ$  decompose into indole and calcium amide. In the preparation about one-half of the indole was reduced to dihydroindole. *Magnesium indole*,



forms needle-shaped, colourless crystals which, although quite soluble in liquid ammonia when freshly prepared, after a time are not completely soluble. This is probably due to a decomposition with the formation of an insoluble product. *Silver indole*,  $C_8H_6NAg, NH_3$ , is an extremely soluble, crystalline compound which exhibits the phenomenon of supersaturation to a marked degree. *Potassium carbazoles*,  $C_{12}H_8NK, 2NH_3$  and  $C_{12}H_8NK, NH_3$ , form very soluble crystals, which lose their ammonia at  $20^\circ$ . *Silver carbazole*,  $C_{12}H_8NAg, 2NH_3$ , is formed at  $-39^\circ$ , and on warming loses one molecule of ammonia to give  $C_{12}H_8NAg, NH_3$ . *Calcium carbazole*,  $(C_{12}H_8N)_2Ca, 7NH_3$ , forms yellow crystals with a green fluorescence at  $-39^\circ$ , and on heating at  $30^\circ$  loses three molecules of ammonia to give  $(C_{12}H_8N)_2Ca, 4NH_3$ .

J. F. S.

**Pyrrole-blacks.** A. ANGELI and CORRADO LUTRI (*Atti R. Accad. Lincei*, 1920, [v], 29, i, 14—22. Compare A., 1919, i, 134).—In presence of water, pyrrole and *p*-benzoquinone rapidly react, giving first a reddish-brown, colloidal solution clearly showing Tyndall's phenomenon and then a black, amorphous powder closely resembling pyrrole-blacks and melanins; the mother liquor contains considerable proportions of quinol. The reaction takes place also in alcoholic, ethereal, or, more slowly, moist benzene solution. If the product of the reaction is washed with water and extracted with alcohol in a reflux apparatus, a black substance is obtained which, when heated, does not melt, but emits vapour which colours red a pine splinter moistened with hydrochloric acid; it dissolves in alkali hydroxide solution, giving an intense brownish-black coloration, but is insoluble in alkali carbonate solution. The percentage compositions of two preparations are: C, 69.14—69.22 (68.75—68.85); H, 2.86—2.90 (2.80—2.84); N, 6.11 (—), and the compound is probably formed by the interaction of 3 mols. and 5 mols., or 4 mols. and 7 mols., of pyrrole and *p*-benzoquinone respectively. The conclusion is drawn that the melanins represent complex molecules

similar to the polysaccharides, polypeptides, polyterpenes, caoutchouc, etc., the tendency to polymerise being due partly to the presence of conjugated double linkings in the pyrrole molecule. Under the same conditions indole does not react with pyrrole.

Similarly, pyrrole and 1:4-naphthaquinone interact, yielding naphthaquinol and a compound,  $C_{34}H_{19}O_5N$  (?), which crystallises in violet-black needles and, when heated, melts incipiently and at the same time emits vapour giving a red coloration to a pine splinter moistened with hydrochloric acid; it is readily decomposed by hot potassium hydroxide solution with formation of an orange-coloured product very sparingly soluble in the ordinary solvents. The compound appears to be formed by the condensation of 1 mol. of pyrrole with 3 mols. of the naphthaquinone.

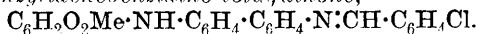
Isatin and pyrrole also react readily (compare Liebermann and Kraus, A., 1907, i, 657).

Oxidation of pyrrole by means of hydrogen peroxide yields (1) a pyrrole-black, and (2) a compound,  $C_8H_{10}ON_2$ , which crystallises in shining, almost colourless needles, m. p.  $136^\circ$ , and at about  $200^\circ$  in presence of air blackens and emits vapour giving an intense red coloration to a pine splinter moistened with hydrochloric acid. By a few drops of dilute sulphuric acid and a trace of dichromate this compound is coloured brown, a black powder being slowly deposited. With nitrous acid or ferric chloride it gives a yellow coloration and, later, a black powder. With a trace of nitroprusside and potassium hydroxide it yields a brilliant violet coloration turned deep blue by acetic acid.

T. H. P.

**Benzidino-quinones and Bisquinonylbenzidines as Vat Dyes.** KURT BRASS and OTTO PAPP (*Ber.*, 1920, 53, [B], 446—462).—Previous attempts to study the primary product of the interaction of benzidine on *p*-benzoquinone (Brass, A., 1913, i, 1232) were rendered difficult on account of the readiness with which it loses a molecule of benzidine to yield quinonebenzidine, which is subsequently readily polymerised. More successful attempts are now described in which substituted quinones are employed.

*Benzidino-toluquinone* is prepared by the action of a solution of benzidine in 50% acetic acid on a hot aqueous solution of toluquinone; it forms a dark violet powder, which is decomposed by prolonged contact with air. By reduction with hyposulphite in very faintly alkaline solution, it yields a yellow vat, from which cotton is dyed in brown shades, which, however, are due to the polymerised form of the dye. The free amino-group shows little tendency to enter into action, but its presence is established by the isolation of *N-p-chlorobenzylidenebenzidino-toluquinone*,



Methylanilino-*p*-benzoquinone condenses with benzidine in alcoholic solution to yield a mixture of 2-benzidino-5-methylanilinobenzoquinone, m. p.  $216$ — $217^\circ$  (corr.) [H. and W. Suida, A., 1919, i, 81, give  $215$ — $218^\circ$ ], and relatively small amounts of *NN'*-bis-5-methylanilinobenzoquinonyl - 2 - benzidine,  $[NMePh \cdot C_6H_2O_2 \cdot NH \cdot C_6H_4]_2$ ,

m. p. 254° (decomp.). The substances have similar tinctorial properties, and dye cotton in yellowish-brown shades from a yellow vat. *2-Di-o-anisidino-5-methylanilinobenzoquinone*,

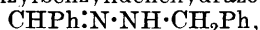
$\text{NMePh} \cdot \text{C}_6\text{H}_2\text{O}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{NH}_2$ , brown leaflets, m. p. 124—128° (decomp.) after softening from 120°, and *NN'-bis-5-methylanilinobenzoquinonyl-2-dianisidine*,  $[\text{NMePh} \cdot \text{C}_6\text{H}_2\text{O}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_3(\text{OMe})]_2$ , brown needles, m. p. 244—246° (corr.), are prepared from methylanilinobenzoquinone and di-o-anisidine, and are separated by taking advantage of the greater solubility of the latter in acetone; on cotton, they yield brown shades with a tendency towards olive.

Another ready method of preparing simple vat dyes consists in the oxidation of anilino-quinones to benzidine derivatives (compare Brass, A., 1912, i, 874); 2-anilino-3:5:6-trichlorobenzoquinone, however, is converted by manganese dioxide in the presence of sulphuric acid into *3'-anilino-2':5':3:5:6-pentachlorodibenzoquinonylaniline*,  $\text{C}_6\text{O}_2\text{Cl}_3 \cdot \text{NPh} \cdot \text{C}_6\text{O}_2\text{Cl}_2 \cdot \text{NHPh}$ , microcrystalline, bluish-grey leaflets, which does not melt below 300° and dyes cotton in dull brown shades.

Whilst benzidine and  $\alpha$ -naphthaquinone yield only 2-benzidino- $\alpha$ -naphthaquinone (Pummerer and Brass, A., 1911, i, 655), it is found that dianisidine, under similar conditions, gives *NN'-bis- $\alpha$ -naphthaquinonyl-2-dianisidine*,  $[\text{C}_{10}\text{H}_5\text{O}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_3(\text{OMe})]_2$ , brownish-violet, crystalline powder, m. p. 303—305°, which dyes cotton in violet shades. In a similar manner, *NN'-bis-3-chloro- $\alpha$ -naphthaquinonyl-2-dianisidine*, red needles, m. p. 270—272°, is prepared from 2:3-dichloro- $\alpha$ -naphthaquinone; it gives brownish-violet shades on cotton. *o*-Ethoxybenzidine and  $\alpha$ -naphthaquinone yield *NN'-bis- $\alpha$ -naphthaquinonyl-3-ethoxybenzidine*,

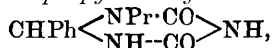
$\text{C}_{10}\text{H}_5\text{O}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_3(\text{OEt}) \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_{10}\text{H}_5\text{O}_2$ , slender, violet-brown needles, m. p. 279—281°, which dyes cotton in violet shades.  
H. W.

**Four-membered Cyclic Ureas. III. Condensation of isoCyanic Acid with Alkyl Schiff Bases and Related Compounds.** WILLIAM J. HALE and NORBERT A. LANGE (*J. Amer. Chem. Soc.*, 1920, **42**, 107—116).—Further investigation shows that the condensation of isocyanic acid with Schiff bases which contain an alkyl group attached to the nitrogen atom proceeds in the same manner as with benzylidene-ethylamine (A., 1919, i, 225). The reaction has been further extended to substances which contain the carbimino-nucleus attached to a nitrogen atom, and, in the special instance of benzylbenzylidenetriazone,



the results obtained confirm those of Bailey and Moore (A., 1917, i, 355).

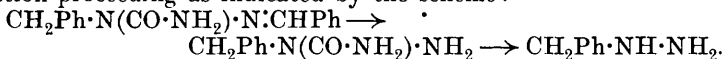
*4:6-Diketo-2-phenyl-1-propylhexahydro-1:3:5-triazine*,



colourless, flaky needles, m. p. 211°, is prepared by the gradual

addition of powdered potassium cyanate to a well-cooled solution of benzylidene-*n*-propylamine in glacial acetic acid; the corresponding *monoacetyl* derivative forms colourless prisms, m. p. 120°. 4:6-*Diketo-2-phenyl-1-butylhexahydro-1:3:5-triazine* is prepared in a similar manner and has m. p. 188°, whilst 4:6-*diketo-2-phenyl-1-amylhexahydro-1:3:5-triazine* has m. p. 202°.

Benzylbenzylidenesemicarbazone (Bailey and Moore, *loc. cit.*) is slowly hydrolysed when treated with steam in the presence of hydrochloric acid to benzaldehyde and benzylhydrazine hydrochloride, the action proceeding as indicated by the scheme:



A mixture of 2-benzylsemicarbazide,  $\text{CH}_2\text{Ph}\cdot\text{N}(\text{CO}\cdot\text{NH}_2)\cdot\text{NH}_2$ , m. p. 135—136°, and 1-benzylsemicarbazide,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ ,

m. p. 155°, is obtained by the cautious addition of potassium cyanate to a concentrated, ice-cold, aqueous solution of benzylhydrazine hydrochloride; the two substances are readily separated by taking advantage of the sparing solubility of the latter in cold chloroform, in which the former is freely soluble (compare Curtius, A., 1910, i, 610; Busch, Opfermann, and Walther, A., 1904, i, 628; Kessler and Rupe, A., 1912, i, 219). The 2-derivative is smoothly transformed into the 1-compound when heated for a few minutes at its melting point.

*α*-Diphenylbenzylidenehydrazine,  $\text{CHPh}\cdot\text{N}\cdot\text{NPh}_2$ , phenylbenzylidenehydrazine, and 2-benzyl-1-benzylidenesemicarbazone could not be caused to condense with *isocyanic* acid. H. W.

**Origin of the Humin formed by the Acid Hydrolysis of Proteins. IV. Hydrolysis in the Presence of Aldehydes. III. Comparative Hydrolysis of Fibrin and Gelatin in the Presence of Various Aldehydes.** GEORGE E. HOLM and ROSS AIKEN GORTNER (*J. Amer. Chem. Soc.*, 1920, **42**, 632—640).—Previous work on the influence of the presence of aldehydes on the nature of the products obtained by acid hydrolysis of proteins (A., 1918, i, 84) has been extended by the hydrolysis of fibrin and gelatin in presence of benzaldehyde, acetaldehyde, butaldehyde, and *iso*-butaldehyde. Whilst the proportions of "ammonia" and soluble humin nitrogen are not appreciably altered, that of acid-insoluble humin nitrogen increases rapidly to a maximum with increase in the quantity of benzaldehyde used. This result is ascribed to the presence of both tryptophan and tyrosine. Butaldehyde and *iso*-butaldehyde are similar in their effects to benzaldehyde, but they give rise to black, insoluble residues, possibly the result of their polymerisation. This change is much more marked in the case of acetaldehyde, and consistent results are therefore not obtained. Whilst the total amino-nitrogen in the filtrate from the soluble humin diminishes rapidly when hydrolysis is carried out in presence of increasing amounts of formaldehyde, probably owing to condensation of formaldehyde with amino-acids, only a slight decrease is

observed when benzaldehyde, or butaldehyde, or *isobutaldehyde* is used. J. K.

**Distribution of Basic Nitrogen in Phaseolin.** A. J. FINKS and CARL O. JOHNS (*J. Biol. Chem.*, 1920, **41**, 375—377).—The average values are: cystine, 0·84%; arginine, 6·11%; histidine, 3·32%, and lysine, 7·88%. The latter value is considerably higher than that obtained by the direct method of Kossel and Patten (*A.*, 1903, ii, 582). J. C. D.

**Effect of Poisons on an Enzymatic Process. V. Alkaloids, Caffeine.** C. G. SANTESSON (*Skand. Arch. Physiol.*, 1919, **39**, 132—166; from *Chem. Zentr.*, 1920, i, 392. Compare *A.*, 1915, i, 728).—In continuation of previous investigations, the influence of the following substances on the power of the catalase of frog's muscle to effect the decomposition of hydrogen peroxide has been studied: pyridine, quinoline, quinine, quinine hydrochloride and hydrobromide, veratrine, veratrine hydrochloride, caffeine, nicotine and its hydrochloride, veratrine (Swedish pharmacopœia), coniine and its hydrochloride, morphine and its hydrochloride, dionine, diacetylmorphine (base and hydrochloride), cocaine (base and hydrochloride), atropine (base and sulphate), strychnine, and aconitine (base and acid hydrochloride). The majority of the free alkaloids, even in very dilute solution, facilitate the action of the catalase to a marked degree, and a similar effect is observed with pyridine; little or no activation is observed only with quinoline, coniine, and caffeine. The alkaloidal salts, on the other hand, generally have a restraining action; nicotine hydrochloride, ethylmorphine (dionine), and atropine sulphate are exceptions in this respect. H. W.

**Composition of Salvarsan.** ROBERT GEORGE FARGHER and FRANK LEE PYMAN (*T.*, 1920, **117**, 370—377).

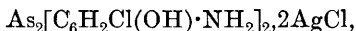
**Silver Salvarsan.** A. BINZ, H. BAUER, and A. HALLSTEIN (*Ber.*, 1920, **53**, [B], 416—428).—From a study of silver salvarsan and allied substances, the authors are led to the following conclusions: (1) colloidal silver is not present in silver salvarsan; (2) two molecules of silver nitrate react with one molecule of salvarsan or its derivative; (3) silver salvarsan contains silver oxide in complex form; (4) Karrer's hypothesis that the silver atoms are united by the residual affinities of the arsenic atoms is not established, since this would indicate a tendency for the latter to pass into the quinquevalent state, whereby they would lose therapeutic power; probably the amino-groups, the capacity of which to take part in complex salt formation is well established, are responsible for the formation of metallic derivatives, or, as recently suggested by Dilthey, the metallic atoms may be united to the molecule as a whole, and not to any particular group.

3-Amino-4-hydroxyphenylarsinic acid is diazotised and converted into 3-chloro-4-hydroxyphenylarsinic acid, which, on nitration, yields 3-chloro-5-nitro-4-hydroxyphenylarsinic acid; the latter is

reduced by hyposulphite to 5:5'-dichloro-3:3'-diamino-4:4'-dihydroxyarsenobenzene, the *dihydrochloride* of which,

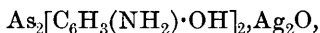


forms greenish-yellow flocks, and is transformed by silver nitrate into *dichlorosalvarsan di-silver chloride*,



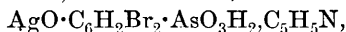
yellow, gelatinous precipitate. The corresponding copper salt,  $\text{As}_2[\text{C}_6\text{H}_2\text{Cl}(\text{NH}_2)\cdot\text{O}\cdot\text{Cu}]_2\cdot\text{CuCl}_2$ , is yellowish-brown.

3:3'-*Diamino-4:4'-dihydroxyarsenobenzene di-silver iodide*,  $\text{As}_2[\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{OH}]_2\cdot 2\text{AgI}$ , is prepared by successive treatment of an aqueous solution of the salvarsan base with hydriodic acid and silver nitrate, and forms an orange-coloured colloidal precipitate. Attempts to convert it into the silver salvarsan base,



by means of sodium carbonate were not completely successful, since oxidation occurred during the washing of the primary black precipitate. When treated with sodium hydroxide, it gives the soluble sodium salt of silver salvarsan, in which the absence of colloidal silver or silver oxide is demonstrated by ultra-filtration experiments, by the absence of the Tyndall phenomenon, and by the appearance under the ultramicroscope. When copper chloride and salvarsan are mixed in aqueous solution, a yellow precipitate of 3:3'-*diamino-4:4'-dihydroxyarsenobenzene mono-copper chloride hydrochloride*,  $\text{As}_2[\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}_2]_2\cdot\text{CuCl}_2\cdot\text{HCl}$ , is obtained.

3:5:3':5'-Tetrabromo-*p*-arsenophenol is mainly oxidised by silver nitrate in pyridine methyl-alcoholic solution, yielding, amongst other products, the *substance*,



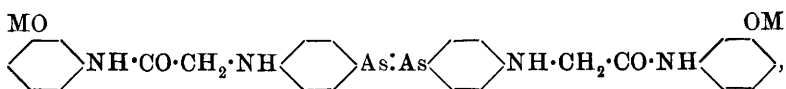
m. p. 157—158°, in which the relative positions of pyridine and silver may possibly be reversed. When a solution of the sodium salt of 3:5:3':5'-tetrabromo-*p*-arsenophenol is treated with silver nitrate, it gives a brown precipitate of *di-silver 3:5:3':5'-tetrabromo-*p*-arsenophenoxide*, which dissolves in sodium hydroxide to a clear brown solution which closely resembles sodium silver salvarsan, but, on ultra-filtration, gives a black residue of colloidal silver and a colourless solution.

Arsenobenzene, conveniently prepared by the reduction of phenylarsinic acid with hypophosphorous acid, has m. p. 208°, whereas Michaelis and Schulte give m. p. 196°. When treated with silver nitrate, it becomes coated with a brownish-black deposit of silver, and is partly transformed into phenylarsinic acid; a somewhat similar phenomenon is observed with gold chloride, but it does not appear to react with copper chloride.

H. W.

**Aromatic Arsenical Compounds.** WALTER ABRAHAM JACOBS, WADE HAMILTON BROWN, MICHAEL HEIDELBERGER, and LOUISE PEARCE (Brit. Pat. 128181; addition to Brit. Pat. 120385. Compare A., 1919, i, 231).—The sodium or potassium salts of the

*N*-(arsenoaryl)bis- $\alpha$ -aminoacylarylamides of the formula



where M is the alkali metal, previously described (*loc. cit.*), are equally valuable for the treatment of trypanosomal or spirochætal infection, and, being soluble in water, are particularly suitable for practical therapeutic use. As an example of their preparation, equivalent quantities of sodium hydroxide and *N*-(arsenophenyl)-bisglycyl-*m*-aminophenol may be dissolved together in water, and the salt isolated either by evaporating to dryness under reduced pressure or by precipitation with a liquid miscible with water, such as acetone or alcohol. It forms a yellow powder, readily soluble in water.

G. F. M.



### Physiological Chemistry.

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**The Equilibrium between Oxygen and Carbonic Acid in Blood.** LAWRENCE J. HENDERSON (*J. Biol. Chem.*, 1920, 41, 401—430).—This paper seeks to explain the interaction between oxygen and carbonic acid in blood by means of the theory of acid-base equilibrium. The isohydric change from fully reduced to fully oxygenated blood, the transfer of base from carbonic acid to hæmoglobin, which is the main feature of this process, and the change of strength, as acid, of a portion of the hæmoglobin molecule, which is its cause, are discussed. It is shown that all these phenomena can be explained by the assumption that a certain acid radicle of the hæmoglobin molecule has, for reduced hæmoglobin and oxyhæmoglobin, respectively, the following values:  $K_R = 2.3 \times 10^{-8}$ ,  $K_O = 2.0 \times 10^{-7}$ . From this consideration, it follows that the salt of the acid radicle in question must have a greater affinity for oxygen than the free acid. If the mass law constants of the reaction of salt and acid with oxygen were  $K_s$  and  $K_f$ , respectively, it should be approximately true that  $K_A/K_s = K_O/K_R = 9$ . In the light of these considerations, the equilibrium between protein acid radicles and base in blood is examined. The bearings of these considerations on Hill's equation for the equilibrium between hæmoglobin and oxygen is considered, but at this point the difficulties are only partly overcome. The union of hæmoglobin as a base with acids, and especially with carbonic acid in blood, is discussed. Finally, the bearing of these considerations on the physiological processes, both the homogeneous reactions within the corpuscles and the plasma, and also the heterogeneous exchanges between corpuscles and plasma, is investigated.

J. C. D.

**Alkalinity of Blood.** RENÉ CLOGNE (*J. Pharm. Chim.*, 1920, [vii], 21, 49—62).—See this vol., ii, 340.

**The Colloidal Chemical Action of Normal Alkali Salts on the Process of Phagocytosis.** W. RADSMÅ (*Arch. Néerland. Physiol.*, 1920, 4, 197—215).—The influence of normal alkali salts on phagocytosis depends both on the cations and the anions. Arranged in descending order of intensity of phagocytosis, the anions are  $\text{Cl}'$ ,  $\text{ClO}_3'$ ,  $\text{Br}'$ ,  $\text{NO}_3'$ ,  $\text{I}'$ ,  $\text{CNS}'$ , and the cations are  $\text{Na}'$ ,  $\text{K}'$ ,  $\text{Rb}'$ ,  $\text{Cs}'$ ,  $\text{Li}'$ , there being very little difference between corresponding salts of sodium, potassium, and rubidium. The action of these salts on the process of phagocytosis must be considered as a lyotropic action. The compounds formed between the protein substances of the protoplasm of the membrane of the leucocytes and the ions mentioned above play no direct part in the mechanism of phagocytosis. The point of action of the salt is not at the interior of the leucocyte, but in the protein substances at the surface of the leucocyte, and the intensity of the phagocytosis is an indicator of the colloidal chemical structure of the protein substances of the protoplasm at this surface. W. G.

**Nutritive Value of the Proteins of the Barley, Oat, Rye, and Wheat Kernels.** THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with the co-operation of ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1920, 41, 275—306).—The proteins of the entire kernel of these grains are adequate for the growth of albino rats, being more efficient for this purpose than the proteins of the endosperm alone. J. C. D.

**Studies in Nutrition. II. The Rôle of Cystine in Nutrition as Exemplified by Nutrition Experiments with the Proteins of the Navy Bean (*Phaseolus vulgaris*).** CARL O. JOHNS and A. J. FINKS (*J. Biol. Chem.*, 1920, 41, 379—389).—Cystine is essential for normal growth. Phaseolin, the principal protein of the navy bean, is rendered a more efficient food by heating with water. Cooked phaseolin or cooked navy bean, when supplemented with cystine, furnished adequate protein for normal growth. J. C. D.

**The Influence of Radioactive Elements on the Development [of Tadpoles].** A. J. P. VAN DEN BROEK (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, 22, 563—567).—Tadpoles in a medium containing a radioactive substance antagonistic to potassium, namely, uranium, grow and metamorphose less quickly than in a medium only containing potassium. There is an indication that the presence of equi-radioactive quantities of the antagonistic substance tends to prevent the absorption of potassium by the tadpole, and there is also some indication of a poisoning effect. W. G.

**Effect of the Chlorine Substitution Products of Methane, Acetaldehyde, and of Sodium Acetate on Catalase Production.** W. E. BURGE and F. L. BURGE (*J. Biol. Chem.*, 1920, **41**, 307—314).—The inhibitory action of chlorine substitution products of methane on catalase action is proportionate to the degree of substitution. Similarly, chloral is more inhibitory than acetaldehyde. The ingestion of sodium acetate causes an increase of catalase, but this is less marked when sodium salts of the chloroacetic acids are used. The chlorine appears to decrease catalase by direct destruction and by decreasing the output from the liver. The increase in oxidation following the ingestion of glycine is attributed to an increase in catalase, whereas the decrease in oxidation during narcosis is attributed to a decrease in the enzyme.

J. C. D.

**Influence of Uranium and Potassium on the Viscosity of Colloidal Liquids.** I. GUNZBURG (*Arch. Néerland. Physiol.*, 1920, **4**, 233—242).—The viscosity of the muscular juice from a frog is above normal in liquids containing less than 25 mg. or more than 100 mg. of uranyl nitrate per litre, there being a point of minimum viscosity at a concentration of approximately 50 mg. of uranyl nitrate per litre. In the presence of potassium chloride, the viscosity remains almost constant at a value below normal for all concentrations of the chloride, although there is indication of a critical point at a concentration of 0.75—1.25 grams of potassium chloride per litre. In the presence of a mixture of the two salts, the viscosity of the muscular juice depends on the relative proportions of the two salts present.

W. G.

**Genesis of Thiocyanic Acid in Animals. IX.** SERAFINO DEZANI (*Arch. Farm. speriment. Sci. aff.*, 1919, **28**, 23—32. Compare this vol., i, 345).—The results of further experiments, together with those already described, lead to the final conclusion that thiocyanic acid is not produced in the animal organism, but is purely exogenetic.

T. H. P.

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## Chemistry of Vegetable Physiology and Agriculture

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### **Biochemistry of the Acetone and Butyl Alcohol Fermentation of Starch by *Bacillus Granulobacter Pectinovorum*.**

HORACE B. SPEAKMAN (*J. Biol. Chem.*, 1920, **41**, 319—343).—*Bacillus granulobacter pectinovorum* growing in a medium rich in starch changes the latter into dextrose by exoenzymic activity. The dextrose then passes into the cell, and is oxidised to acetic and butyric acids, which are reduced in part to the corresponding alcohols.

J. C. D.

**Fermentation of Lævulose by *Lactobacillus pentoaceticus*, N. Sp.** W. H. PETERSON and E. B. FRED (*J. Biol. Chem.*, 1920, **41**, 431—450).—These organisms, which are closely related to the so-called "mannitol bacteria," will attack lævulose, with the production of acetic and lactic acids, mannitol, and carbon dioxide. As much as 30 to 40% of the lævulose may be converted into mannitol in the early stages of the fermentation, but if the process is allowed to go on for a long time, this product is slowly attacked, with the formation of acetic and lactic acids. The same organisms will decompose calcium and sodium malates, with the formation of carbon dioxide and lactic and acetic acids. It is suggested that malic acid may be an intermediate product in the fermentation of the lævulose. J. C. D.

**Chemistry of Alcoholic Fermentation.** CARL NEUBERG and ELSA REINFURTH (*Ber.*, 1920, **53**, [B], 462—469).—The results obtained recently by Zerner (this vol., i, 350) are in general agreement with the older data of Neuberg and his co-workers. Zerner, however, attributes the impossibility of effecting complete conversion of sugar into glycerol and acetaldehyde to a comparatively slow union of the latter with the bisulphite; the work of Kerp shows, on the other hand, that the union is rapid, whilst, in addition, the importance of the development of alkali hydroxide ( $\text{Me}\cdot\text{CHO} + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} = \text{Me}\cdot\text{CH}(\text{OH})\cdot\text{O}\cdot\text{SO}_2\text{Na} + \text{NaOH}$ ) has been completely overlooked. Further, Zerner's conclusion that pyruvic acid cannot be the preliminary stage in the formation of acetaldehyde is based on an erroneous interpretation of an unsuitably devised experiment; absence of evolution of carbon dioxide from a fermenting solution of potassium pyruvate in the presence of a molecule of normal sodium sulphite is to be expected, since reaction occurs in accordance with the scheme  $\text{COMe}\cdot\text{CO}_2\text{K} + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{OH}\cdot\text{CHMe}\cdot\text{O}\cdot\text{SO}_2\text{K} + \text{Na}_2\text{CO}_3$ . The action is also complicated by the fact that fermentation occurs within the living yeast cell, which is now shown to be impermeable to normal sodium sulphite, so that the union of the latter with the aldehyde must occur outside the cell. H. W.

**The Biochemical Production of Pyruvic Acid.** A. FERNBACH and M. SCHOEN (*Compt. rend.*, 1920, **170**, 764—766. Compare A., 1913, i, 231; 1914, i, 237, 910).—Further evidence is given of the formation of pyruvic acid by yeast during alcoholic fermentation. An essential condition for its production is that the medium should be kept neutral, which is best done by the addition of calcium carbonate. Thus, by a change in the reaction of the medium, a change is produced in the nature and relative proportions of the products formed. The formation of pyruvic acid also requires that the medium shall be an inorganic one. W. G.

**The Significance of the Peroxydase Reaction with Reference to the Viability of Seeds.** J. S. MCHARGUE (*J. Amer. Chem. Soc.*, 1920, **42**, 612—615).—Although it has been suggested

that tissues or organs are dead if they fail to show the reactions of peroxydases and oxydases, the author has observed that dead grains, for example, lettuce seed, which failed to give the former reaction, contained a catalase which decomposed hydrogen peroxide; but evidence is adduced to show that the peroxydase reaction is only given by viable seed, and that the intensity of the reaction can be used to distinguish between seeds of low, medium, and high viability. The reaction failed with samples of corn, hemp seed, tomato seed, tobacco seed, oats, cowpeas, soja beans, castor beans, and lettuce seed, which all showed zero germination. Moreover, the temperature at which the blue colour disappeared increased with viability of the seed, although it varied somewhat with the species. Further, the peroxydase reaction was given by the germ, but not by the endosperm, of corn; but when the separation and grinding preparatory to the test were performed under water or alcohol, the germs also gave only a faint reaction, showing that they contain a substance, presumably an oxygenase, which, on exposure to air, rapidly absorbs oxygen, forming the peroxydase. Of the twenty species examined, only soja beans, lucerne, and lettuce seeds contained both oxydases and peroxydases; the respective reactions in each case were both pronounced, weak and strong, intense and moderate. J. K.

**Carbon Monoxide a Product of Respiration.** SETH C. LANGDON and WALTER R. GAILEY (*J. Amer. Chem. Soc.*, 1920, **42**, 641—646).—The conditions under which carbon monoxide is produced in the pneumatocyst (floater) of the giant Pacific Coast kelp, *Nereocystis leutkeana* (A., 1917, i, 372), have been more closely examined. It is not a result of decay or due to the action of enzymes, because finely ground kelp in contact with sea-water gives carbon dioxide and hydrogen only. When the lower part of the stipe was cut away, and the upper part closed with a cork and suspended in the sea after being filled with a gas of known composition, the plant continued to live and grow. When air was used, carbon monoxide was produced, irrespective of whether the fronds had been removed or not, or whether the plant was kept in the light or in the dark, and whatever sections of the stipe were employed. With nitrogen or hydrogen, however, no carbon monoxide was produced, but several per cent. of carbon dioxide were produced. Finally, carbon monoxide was only generated in the living plant. It is therefore considered to be a respiration product rather than an intermediate product in photosynthesis. J. K.

**Influence of the Pyrrole Nucleus in the Formation of Chlorophyll. II.** B. ODDO and G. POLLACCI (*Gazzetta*, 1920, **50**, i, 54—70. Compare A., 1915, i, 1083).—Previous publications on this subject having been discussed, the preparation of magnesium pyrrole-2-carboxylate, and experiments on the influence of nutrient solutions containing this compound on the growth of various plants, are described.

*Magnesium pyrrole-2-carboxylate*,  $\left[ \begin{array}{c} \text{CH}-\text{CH} \\ | \quad \diagup \\ \text{CH}-\text{NH} \end{array} > \text{C} \cdot \text{CO}_2 \right]_2 \text{Mg} \cdot 2\text{H}_2\text{O}$ ,

obtained by heating an aqueous-alcoholic solution of pyrrole-2-carboxylic acid (2 mols.) with magnesium oxide (1 mol.), crystallises in brush-like aggregates of needles or stellar aggregates of leaflets, and begins to decompose at about 260°.

The culture experiments were made with *Zea mays*, *Solanum nigrum*, *Datura stramonium*, *Euphorbia* sp., and *Aster sinensis*, the culture liquids containing calcium nitrate, ammonium sulphate, potassium nitrate, and potassium dihydrogen phosphate (or magnesium pyrrole-2-carboxylate), all carefully purified from traces of iron. The results show that, in the nutrient solutions containing the pyrrole compound, the plants exhibit normal growth, whereas in those free from this compound, plants are obtained with leaves showing marked chlorosis.

Thus, plants grown in a nutritive medium containing an assimilable pyrrole derivative form chlorophyll, even in absence of iron. When no such pyrrole derivative is present, iron constitutes an indispensable element in order that the plastids may become green, and acts, indeed, as a catalyst in the formation of the pyrrole nucleus, which constitutes the centre of the whole chlorophyll complex. Pyrrole and magnesium are, then, the substances which cause plants to become green.

T. H. P.

#### **Influence of certain Organic Compounds on the Development of Plants. IV.** G. CIAMICIAN and C. RAVENNA (*Atti R. Accad. Lincei*, 1920, [v], 29, i, 7—13. Compare A., 1919, i, 241).

—Further experiments have been made with bean plants watered with 0.1% solutions of various compounds. Of the normal amines, methylamine is the least toxic, whilst the toxicity diminishes continuously in passing from ethylamine to *n*-amylamine; the action is manifested by the appearance of yellow, translucent spots on the leaves, the plants being killed by ethylamine and rendered less vigorous by the other amines. *iso*Amylamine is somewhat more poisonous than *n*-amylamine, and determines a characteristic albinism of the compound leaves, which are deprived of chlorophyll either entirely or everywhere but along the principal veins; this albinism recalls that due to nicotine, which is accompanied by *iso*amylamine in tobacco. Potassium *n*-butyrate is without apparent effect, whereas the *isobutyrate* causes partial falling of the leaves.

Formamide causes fall of the seed-leaves, probably owing to the presence of the aldehydic group, whilst acetamide is completely innocuous. Oxalic acid causes less vigorous growth than succinic acid. Methyl and, especially, ethyl tartrates produce on the seed-leaves translucent spots, which lead to slow desiccation of the plants. Pyridine allows the plants to develop normally, but picoline produces yellow spots on both the seed-leaves and the compound leaves, without, however, injuring the plants seriously. The influence of the introduction of methyl groups into a molecule

is exhibited more markedly with derivatives of piperidine, which itself is only slightly toxic, whereas 1-methylpiperidine and coniine are highly toxic. Quinoline, *isoquinoline*, and 2-methylquinoline are all intensely toxic, the last more so than the first two, the effects of which are equal. Cocaine kills the plants, ecgonine and the methyl ether of norecgonine produce brown spots on the seed-leaves, but do not prevent further development, although with the former this is restricted; norecgonine produces no apparent effect. Unlike tetramethylammonium salts, betaine is only slightly toxic, producing merely partial withering of the seed-leaves.

With broad bean, pumpkin, and tomato plants, less marked effects are obtained than with beans, but those substances which act most intensely on the latter affect these three plants similarly.

Certain substances, especially morphine and catechol, give an exceptionally dark green colour to the leaves, but the absorption spectra of alcoholic extracts of such leaves exhibit no qualitative difference, but only a different intensity of absorption from those obtained with normal leaves; photometric measurements indicate the presence of twice as much chlorophyll in the former as in the latter leaves, but the proportion of starch present is no greater. Thus the quantity of starch present is not related to the intensity of the green colour of the leaves, and although most of the toxic substances examined favour the deepening of the colour, some, such as theobromine, produce the opposite effect.

The toxic substances investigated do not merely act on the roots, but pass into the tissues of the plant. With catechol, however, no trace is detectable in the plant, this compound being probably destroyed by enzymic action (compare A., 1918, i, 93).

T. H. P.

### **The Lipolytic Activity of the Castor and Soja Bean.**

ARTHUR WILLIS BARTON (*J. Amer. Chem. Soc.*, 1920, **42**, 620—632).—Preliminary to a study of the activity of the lipases of castor and soja beans, it was shown that Falk's method of determining the liberated fatty acids (A., 1912, i, 522) is inapplicable when lard or olive oil is used as a substrate; complete neutralisation is only achieved by the addition of alcohol and ether to produce a homogeneous solution before titration with aqueous alkali hydroxide. In the case of castor beans, the husks were removed for the preparation of the lipase, because its activity was in this way doubled, but this was unnecessary with soja beans. From his results the author deduces that (1) castor bean lipase is more intense in its action than soja bean; (2) the ranges of acidity of medium in which action on lard and olive oil takes place are practically the same for the two lipases (0.0—0.5% hydrochloric acid), and are independent of the substrate; (3) the degree of activity for a given acidity is practically the same for olive oil and for lard, the maximum for castor bean being at 0.2% and for soja bean at 0.4%; (4) the activity towards ethyl butyrate is less, and the range of acidity in which



action takes place is much higher and shorter. It is concluded that soja and castor beans contain more than one, but the same, lipases.

J. K.

**Proso Millet—Analysis of the Oil—a Characteristic Alcohol.** B. A. DUNBAR and E. R. BINNEWIES (*J. Amer. Chem. Soc.*, 1920, **42**, 658—666).—The oil extracted from proso millet, *Panicum miliacum*, by ether or light petroleum gradually deposits thin, pearly-white plates, m. p.  $279^{\circ}$  (corr.), soluble in most organic solvents, but sparingly in cold ether or alcohol. As it could not be identified, it was called "*prosol*." It has the formula  $C_{24}H_{36}O_2$ , can be acetylated, and with hydroxylamine gives an unsatisfactory quantity of a precipitate, presumably an oxime. The formation of a fluorescein, under conditions vaguely specified, is looked on as evidence of a ring structure, with two side-chains in the ortho-position. The oil itself is a semi-drying oil, comparable with rape-seed oil. [For analytical details, see *J. Soc. Chem. Ind.*, 1920, .]

J. K.

**Chemical Examination of the Root of Nerium Odorum (Kanhher).** SHUNKER TRIMBAK GADRE (*J. Ind. Inst. Sci.*, 1916, **1**, 181—199).—The air-dried roots of *Nerium Odorum* collected in winter in the Krishna valley, when extracted with hot alcohol, lost 13.7% of their weight. The alcoholic extract, when distilled in steam, yielded a small amount of an orange-coloured essential oil, having  $D_4^{30}$  0.8660;  $[\alpha]_D^{31}$   $-4.088^{\circ}$ ;  $n_D$  1.40315. Of the total residual extract, 45% was soluble in water, and this aqueous solution contained a small amount of a crystalline phenolic compound, m. p.  $140-141^{\circ}$ , a considerable amount of a glucoside, and free dextrose. The portion of the extract insoluble in water, constituting 7.5% of the original root, was composed of a hard and a soft resin. From the hard resin the author isolated formic and butyric acids in traces, oleic, linolic, palmitic and stearic acids, a new alcohol, *kanerol*,  $C_{30}H_{50}O$ , m. p.  $185.7-186.2^{\circ}$  (corr.),  $[\alpha]_D^{30}$   $+80.1^{\circ}$ , giving an *acetyl* derivative, m. p.  $208-210^{\circ}$ ,  $[\alpha]_D^{30}$   $+84.88^{\circ}$ , and a *benzoyl* derivative, m. p.  $189-190^{\circ}$ . In addition, the hard resin contained a small quantity of an aromatic acid, m. p.  $243-245^{\circ}$ . The soft resin contained oleic, linolic, palmitic and stearic acids, and the alcohol *kanerol*, which gave the colour reactions for a phytosterol, and in most respects closely resembled  $\alpha$ -amyrin.

The ethyl acetate and the alcohol extracts of the hard resin were found to consist mainly of resin acids.

W. G.

**Okra Seed Oil.** GEORGE S. JAMIESON and WALTER F. BAUGHMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 166—170).—The chemical characteristics of four samples of the cold-pressed oil from okra seed (*Abelmoschus esculentus*, Malvaceæ) have been determined. These oils vary somewhat in composition. A recently expressed oil contained the glycerides of palmitic acid (27.23%), stearic acid (2.75%), arachidic acid (0.05%), oleic acid (43.74%), linolic acid (26.62%), and unsaponifiable matter (0.37%).

H. W.

**Pimpernel Saponin.** CONRAD VESTLIN (*Pharm. Zentr.-h.*, 1920, **61**, 77—78).—Roots of *Pimpinella saxifraga* germ. yielded 1·107% of a saponin having the formula  $C_{23}H_{36}O_{18} \cdot 2H_2O$ .

W. P. S.

**Hydrocyanic Acid Content of Phaseolus lunatus. II.** H. LÜHRIG (*Chem. Zeit.*, 1920, **44**, 262. Compare this vol., i, 359).—Further experiments on hydrocyanic acid in *Phaseolus lunatus* beans showed that treatment of the beans with saliva did not increase the amount of hydrocyanic acid above that formed by the action of the natural enzyme of the beans; prolonged action of saliva tended to reduce the amount of hydrocyanic acid. The residues remaining after the removal of the hydrocyanic acid by distillation were treated with emulsin, saliva, bile, and pancreatic juice, but no further amount of hydrocyanic acid was obtained.

W. P. S.

**Urease of the Seeds of Robinia pseudacacia.** P. Y. YI (*Ber. deuts. pharm. Ges.*, 1920, **30**, 178—191).—The quantity of ammonia liberated in the enzymic decomposition of urea by the powdered seeds of *Robinia pseudacacia* increases proportionately with the amount of seed powder used and the duration of the action, and the decomposition is accelerated by raising the temperature to 37°. The most active preparations of the urease are obtained by precipitation with alcohol from an aqueous extract of the seeds, although this causes some injury to the enzyme. Lead acetate, sodium chloride, and ammonium sulphate are still less suitable precipitants. When salt solutions of equal concentration are used, the most energetic action on urea is obtained with sodium acetate solution. Pure water dissolves most urease at 40°, the activity of the aqueous solutions decreasing with the rise in temperature, and practically ceasing at 80°. The fact that the urease of *Robinia* seeds is only partly soluble in water supports the view that two or more ureases differing in physical properties are present. *Robinia* urease decomposes *as*-dimethyl- and diethyl-carbamides, but has little, if any, action on the corresponding symmetrical compounds.

C. A. M.

**The Hydrocyanic Acid Question. IV. The Seeds of Schleicheria trijuga.** L. ROSENTHALER (*Schweiz. Apoth. Zeit.*, 1920, **58**, 17—20; from *Chem. Zentr.*, 1920, i. 338. Compare this vol., i, 130).—Uncombined hydrocyanic acid is not present in the seeds of *Schleicheria trijuga*, Willd.; a compound of it, however, can be removed from the oil with ether or light petroleum, which is not identical with amygdalin, phaseolunatin, or linamarin. It does not appear to be a glucoside, but is possibly a hydroxynitrile.

H. W.

**The Function of Vitamines in the Metabolism of Sclerotinia cinerea.** J. J. WILLAMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 549—585).—The solutions found by Currie (A., 1917, i, 614) to promote the growth of *Aspergillus niger* failed when

applied to the case of *Sclerotinia cinerea* (Bon.), Schröter, the brown rot organism of peaches and plums, but normal development took place when small amounts of peach, prune, or apple juice were added, that of the first being most effective. A variety of nitrogen compounds, sugars, pectin, and salts of organic and inorganic acids were also ineffective when not contaminated with mother liquors from a plant juice. It is therefore suggested that the vitamins present in the juices are responsible for their influence.

By means of adsorption with fuller's earth, vitamin preparations were made from many and most varied sources, both plant and animal. All these preparations were active in promoting growth of *Sclerotinia*; a few of them also promoted reproduction.

Some experimental evidence was obtained favouring the view that there might be two separate vitamin factors involved in the two phases, vegetation and reproduction, but, on the other hand, the hypothesis of but a single vitamin for *Sclerotinia* is more plausible and accords with much of the experimental evidence, and it is very probable that reproduction in *Sclerotinia* is simply a different manifestation of the same activities as characterise vegetation. The *Sclerotinia* vitamin is possibly identical with water-soluble B of the higher animals.

J. K.

**Composition of Hubbard Squash Seed Oil.** WALTER F. BAUGHMAN and GEORGE S. JAMIESON (*J. Amer. Chem. Soc.*, 1920, **42**, 152—157).—The seeds of *Cucurbita maxima* contained 5.72% of moisture and 36.66% of matter soluble in ether. The cold, pressed oil had  $D_{20}^{25}$  0.9179,  $n_D^{25}$  1.4714, iodine number (Hanus) 121.0, saponification number 191.5, Reichert-Messel number 0.37, Polenske number 0.39, acetyl number 27.8, acid number 0.50. Chemical examination showed the presence of the glycerides of palmitic acid (13%), stearic acid (6%), arachidic acid (trace, about 0.04%), oleic acid (37%), and linolic acid (44%). The unsaponifiable matter amounted to 1%.

H. W.

### **Nicotine in Tobacco : Genesis and Function of Alkaloids.**

LUIGI BERNARDINI (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 62—66).—The results of the author's experiments are as follows. Nicotine is not present in the seed of the tobacco plant, and is harmful to its germination, as also are larger doses of other compounds which contain heterocyclic nuclei and are related chemically to nicotine, such as pyridine and picoline. The alkaloid appears in the young plant immediately the chlorophyll begins to function, and originates in the leaves. The plant, which in its normal development contains the nicotine in its elaborating organs in virtue of the greater vital activity there developed, responds to any serious traumatic lesion, such as cutting, which attacks it at an important stage of its vegetative cycle, the alkaloid being thereby produced in increased quantity and localised in the regions adjacent to the lesion. The localised nicotine of the roots, and especially that accumulated in the leaves, is not utilised by the

plant even when the latter is placed in conditions favourable to such utilisation.

These results lead to the assumption that the nicotine, probably formed from certain residues of the nitrogen katabolism, is elaborated by the plant in order either to prevent accumulation of such residues in the organism or to utilise them, with intensification of their harmfulness, in defence of its organs. An analogous case is that of tannin, which is elaborated by plants to prevent accumulation of polyhydric phenolic residues; the tannin is perhaps more injurious than these residues, but it may be utilised by the plant, being localised, by a simple mechanism, in the wood for its formation and preservation. T. H. P.

### **Urea and other Sources of Nitrogen for Green Plants.**

T. BOKORNY (*Pfluger's Archiv*, 1918, **172**, 466—496; from *Physiol. Abstr.*, **4**, 57).—Green plants are capable of disintegrating and utilising almost as many organic substances as the fungi are. Urea in an initial concentration of 0.05% has a beneficial action on the germination of wheat, and acts as nutrient to the seedlings. 0.1% has a harmful action. J. C. D.

**Effect of Lime on the Sodium Chloride Tolerance of Wheat Seedlings.** J. A. LEClerc and J. F. BREAZEALE (*J. Agric. Res.*, 1920, **18**, 347—356).—As a result of water culture and sand culture trials with wheat seedlings, it is shown that very small amounts of calcium oxide or sulphate overcome the toxic effects of sodium chloride or sulphate. Magnesium sulphate and barium chloride are slightly antagonistic to sodium chloride, but potassium chloride, sodium nitrate, sodium phosphate, ferric chloride, and alum have no effect on the toxicity of sodium chloride.

Under the experimental conditions, the presence of lime did not prevent the entry of sodium chloride or sulphate into the plant, the antagonistic effect of lime not being due, apparently, to its effect on the permeability of the cells, but to some other cause.

The higher tolerance to alkali salts shown by plants in soil or sand cultures as compared with those grown in water cultures is not due entirely to the physical effects of the presence of solid particles of different degrees of fineness, but also to certain soluble substances which are sometimes present in very small quantities.

W. G.

**Enzymes. III. Invertase and other Enzymes of Germinated Barley.** D. MAESTRINI (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 509—511. Compare this vol., i, 273).—Germinated barley dried at temperatures below 40° contains invertase, extractable by 0.003 mol. % acetic acid solution, and present, not only in the emulsion, but also in the filtrate of the extract; the enzyme acts best at about 50°, and is destroyed at 55°. The extract of the germinated barley contains no maltase, lactase, or rennase, the coagulation of milk produced by the extract being due solely to the acidity of the latter, as it is effected even by the boiled extract. A catalase and an oxydase are, however, present in the germinated barley. T. H. P.

**Constituents of Protein in Polished Rice.** JUNZO KUROSAWA (*J. Tokyo Chem. Soc.*, 1919, **40**, 551—561).—In connexion with the nutritive value of various proteins, the nature of the rice protein has been reinvestigated. Dry, pure, polished rice contains 1.77% of total nitrogen, 1.14% of protein nitrogen, 0.13% of non-protein nitrogen, and 7.125% of total protein (=protein nitrogen  $\times$  6.25). The protein nitrogen contains 97.82% soluble in hot hydrochloric acid, 97.81% soluble in hot 30% sulphuric acid, 3.58% of humin (I) nitrogen, 9.20% of ammonia nitrogen in sulphuric acid, 1.18% of humin (II) nitrogen, 20.40% of nitrogen precipitated by acid, and 63.12% of other nitrogen in sulphuric acid. Of the total nitrogen, 10.89% is attributable to arginine, 8.89% to histidine, and 2.67% to cystine; these amounts are quite different from those recorded by other investigators. Cystine corresponds with 0.87%, tyrosine with 3.51%, and tryptophan with 0.88%, calculated on the dry material.

Matsui's observation is confirmed that guanidine nitrogen is eliminated in the Van Slyke method if the reaction is allowed to proceed for several hours.

CHEMICAL ABSTRACTS.

**Enzyme Action. XVIII. The Saccharogenic Actions of Potato Juice.** GRACE MCGUIRE and K. GEORGE FALK (*J. Gen. Physiol.*, 1920, **2**, 215—227. Compare A., 1919, i, 426).—The marked action of the juice alone and also in the presence of added starch at  $p_H$  4 to 5 is due to the hydrolysis of sucrose or raffinose by the sucrase present. There is very little degradation of starch. At  $p_H$  6 there is action both on the part of the sucrase and the amylase, whilst at  $p_H$  7 to 8 the action of the amylase is alone observable.

J. C. D.

**Nutritive Factors in Plant Tissues. III. Further Observations on the Distribution of the Water-soluble Vitamine.** THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with the co-operation of ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1920, **41**, 451—468).—An attempt to place our knowledge of the value of certain foodstuffs as sources of the accessory factors on a quantitative basis. Lucerne and clover are extraordinarily rich in water-soluble *B*. Of the ordinary vegetables, tomatoes appear to be richest, whilst spinach, cabbage, turnip, and carrot are not quite so potent. The beetroot is not equal in this respect to the other roots tested, and Timothy hay also proved disappointing. The potato is evidently rich in the water-soluble *B* factor, which does not appear to be concentrated to any extent in the surface layers. No differences were noted in the food value of old and new potatoes.

J. C. D.

**Salt and Alkaline Soils. Origin of Sodium Carbonate in Soils.** A. DE DOMINICIS (*Staz. sperim. agrar. Ital.*, **51**, 103—161; from *Chem. Zentr.*, 1918, ii, 982—983).—In considering the problem of irrigation of southern soils, account must be taken of

the relationship between irrigation, movement, distribution, and transformation of the neutral sodium salts. Incautious irrigation frequently defeats its purpose, since it results in raising the subterranean salt water, concentration of the salts in the surface layers, and formation of sodium carbonate instead of neutral salts; the occurrence of the carbonate renders the soil less fit for cultivation than does that of neutral salts. The carbonate can be removed by simple washing with water, but this involves the loss of all colloidal mineral and organic substances. Double decomposition between sodium chloride or sulphate and calcium carbonate plays little, if any, part in the production of sodium carbonate. This is shown by the fact that the presence of sodium chloride and sulphate hinders the formation of the carbonate, the latter only appearing after removal of the neutral salts, and being formed to a greater extent in proportion as the removal is more thorough. Nevertheless, an alkaline soil is indirectly dependent on a salt soil. The phenomenon is explained by Gedroiz on the assumption that sodium chloride and sulphate form peculiar compounds in the soil, which can only enter into reaction after removal of the salts to which they owe their origin. These are regarded as absorption compounds, and as being formed by double decomposition between absorbed substances, such as compounds of calcium and magnesium and sodium chloride and sulphate. The extent of the formation of sodium carbonate depends on the intensity and length of action of the neutral salts and on the content of adsorbed sodium which can be extracted with 10% hydrochloric acid.

The author's experiments lead him to a quite different conception of the action. The alkalinity depends primarily on absorbed sodium, but results from the hydrolysis of the "absorbates" when they leave the state of coagulation; the sodium hydroxide so formed can then react with calcium carbonate, but, more commonly, is converted into sodium carbonate by carbon dioxide. Actually, an alkaline reaction can be observed in the absence of calcium carbonate and carbon dioxide. The part played by the neutral salts consists in holding the absorbates in a coagulated condition, in which they are not hydrolysed. The action of gypsum in improving an alkaline soil does not consist in simple neutralisation of sodium carbonate. The carbonate and bicarbonate derived from it, together with the excess of gypsum, coagulate the colloids and change them again into calcium adsorbates, the action being facilitated by the presence of neutral sodium salts. The latter can themselves act helpfully in the removal of alkalinity, but only indirectly and in virtue of the corresponding anions. The prescribed irrigation with salt water is dangerous for the soil, since it inhibits the formation of sodium absorbates; the danger could, however, be avoided by simultaneous treatment with gypsum.

Organic compounds play a part in the formation of sodium carbonate in the soil. Among colloidal mineral substances, those of zeolitic nature, which by double decomposition can yield absorbents, are active; of these, the chabasite type, corresponding with

aluminium silicate, is the most important, whilst substitution occurs very slowly and dissociation takes place with greater difficulty with substances of the natrolitic type. H. W.

**Absorption of Lime by Soils.** F. J. WARTH and MAUNG PO SAW (*Mem. Dept. Agric. India*, 1919, 5, 157—172).—A study of the absorption by different types of soils of calcium carbonate from solutions of calcium hydrogen carbonate at different concentrations and in the presence of varying amounts of carbon dioxide. On the results, a method for estimating the lime requirements of a soil is based and described. W. G.

**The Action of Lime in the Soil.** JOHN HUGHES (*J. Bath & W. & S. Co. Soc.*, 1919, [v], 13, reprint, 10 pp.).—A study of the rate of carbonation of calcium oxide when mixed with four times its weight of soil (*a*) in the air-dry state, (*b*) kept moist with water and placed outdoors. Two types of soil were used, one containing 3.85% and the other 14.97% of organic matter and combined water. In both soils, which were exposed to the air in a moist state, the whole of the calcium oxide was carbonated within six weeks. The author discusses the results of Voelcker's experiments carried out at Woburn on the lime-magnesia ratio in soils. The lime and magnesia contents of eleven Herefordshire soils are given, and in all cases where the magnesia was in excess of the lime, full-crop results were not obtained. W. G.

**The Relation of certain Acidic to Basic Constituents of the Soil affected by Ammonium Sulphate and Sodium Nitrate.** L. P. HOWARD (*Soil Sci.*, 1919, 8, 313—321).—The soils used were from permanent experimental plots which for the last twenty-five years have received, respectively, ammonium sulphate and sodium nitrate, half of each plot being limed. An exchange of bases, produced by treatment of the soil with a solution of potassium chloride, showed a marked degree of reserve acidity from the unlimed soil receiving ammonium sulphate. This acidity, so developed, showed a correlation with the acidity of an aluminium salt equivalent in amount to the weight of aluminium found in the extract. Digestion with hydrochloric acid showed that the quotient obtained by dividing the sum of the weights of the oxides of aluminium and iron by the sum of the weights of the oxides of calcium and magnesium ranged from 85 in the case of the unlimed soil receiving ammonium sulphate to 10 where lime and sodium nitrate were applied. Thus in these acid unlimed soils, iron and aluminium partly took the places occupied by calcium and magnesium in the limed soils. The soil solution acts as a buffer solution containing phosphates and carbonates, and the hydrogen-ion concentration in the soil solution from the unlimed plot receiving ammonium sulphate was very similar to that produced by the addition of even quite large amounts of aluminium salts to buffer solutions. W. G.

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## Organic Chemistry.

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### The Chemical Mechanism of Organic Rearrangements.

ARTHUR MICHAEL (*J. Amer. Chem. Soc.*, 1920, **42**, 787—821).—A theoretical paper dealing with rearrangement as determined by the affinity, energy, and spatial relationships of the atoms involved. Intramolecular rearrangements are determined by the free chemical energy at the interchanging atoms or groups, their affinity for each other and for the atoms in the groups to which they migrate, the amount of energy required to separate the migrating portion from the remaining atoms of the group, and the heats of formation of the isomerides or the two products. In a heterogeneous chemical system, change in chemical structure of a compound may be due to catalytic influence or to chemical action of the energy in the reagent employed, involving loss of a component part of the compound and subsequent isomerisation of the residual structure. A polymolecule may be produced by union of the compound with the reagent, when, owing to the chemical energy so added, isomerisation in the compound portion of the product takes place, resulting in partial conversion of its free energy into bound energy and heat, and subsequent decomposition of the system into the isomerised product and the reagent. These considerations are applied to critical reviews, which do not lend themselves to abstraction, of the various hypotheses proposed in explanation of the Hofmann conversion of bromoamides into primary amines, the rearrangements of aliphatic and aromatic  $\alpha\beta$ -glycols under the influence of acid, the pinacol change, the rearrangements of aryl iodohydrins, and the formation of benzoic acid from benzil. A general consideration is also given of the production of intermediate products in such reactions. In regard to the question as to whether elimination of groups of atoms, for example, hydrogen and bromine from ethyl bromide, takes place from the same carbon atom or from more than one, it is concluded that, generally speaking, the former is of rare occurrence, because the latter usually results in a greater increase in entropy.

J. K.

### Oxidative Decomposition of Hydrocarbons. H. HEINRICH

FRANCK (*Chem. Zeit.*, 1920, **44**, 309—310).—Aliphatic hydrocarbons of high molecular weight, such as paraffin oils and waxes, are oxidised to carboxylic acids and other oxidation products when decomposed by heat in the presence of oxygen and a catalyst. By varying the conditions of the oxidation, different proportions of volatile and non-volatile fatty acids may be obtained. Good results are obtained by the use of compounds of lead, mercury, manganese, vanadium, and chromium as catalysts, whilst alkalis and alkaline earths may also be used. In practice, good yields of fatty acids, ranging from acetic to arachidic acid, may be obtained by heating



paraffin wax in an autoclave at  $150^{\circ}$  in the presence of oxygen and 0.5 to 5% of catalyst, although eventually the oxidation may also be effected without a catalyst. The resulting fatty acids were separated by converting them into esters, which were fractionally distilled. The product obtained from an expressed paraffin-wax residue yielded 57.1% of fatty acids of lower molecular weight and 40.7% of acids of higher molecular weight, and contained unsaponifiable matter, from which a ketone melting at  $46-50^{\circ}$ , probably a mixture of stearone with other ketones, was separated. An edible fat resembling coconut oil was prepared by esterifying the mixed fatty acids thus obtained with ethylene glycol and 3% of sulphuric acid. [See, further, *J. Soc. Chem. Ind.*, 1920, 395A.]

C. A. M.

**Brodie's Myricyl Alcohol.** ALBERT GASCARD (*Compt. rend.*, 1920, 170, 886—888).—Brodie attributed to the myricyl alcohol obtained from beeswax the formula  $C_{30}H_{61}\cdot OH$ . The author has prepared this alcohol and the corresponding iodide, and from careful analyses of the latter, and by preparation of the corresponding saturated hydrocarbon and comparison of the properties of the alcohol and its derivatives with known compounds in a near position in the same series, he concludes that myricyl alcohol has the formula  $C_{31}H_{63}\cdot OH$ . Finally, from lacceric [dotriacontanoic] acid,  $C_{32}H_{65}\cdot CO_2H$  (A., 1914, i, 1045), he has prepared myricyl alcohol by degradation, and from myricyl alcohol, by conversion into the cyanide and hydrolysis, obtained lacceroic acid.

W. G.

**The Equation of State of Ethyl Ether.** E. ARIÈS. (*Compt. rend.*, 1920, 170, 871—875).—By the use of equations already established, the author has calculated the saturated vapour pressures and the differences of the molecular volumes of the saturated fluid for ethyl ether for each  $10^{\circ}$  from  $-10^{\circ}$  to  $190^{\circ}$ , and his results are in fairly close agreement with those obtained by Young. Finally, he finds for the heat of vaporisation of ethyl ether at  $30^{\circ}$  the value 85.63 cal., the value given by Young being 85.18 cal.

W. G.

**The Decomposition of Nitric Esters by Lime.** THOMAS MARTIN LOWRY, KENDALL COLIN BROWNING, and JOSHUA WILLIAM FARMERY (T., 1920, 117, 552—561).

**Action of the Normal Methyl and Ethyl Sulphates on the Alkali Phosphates in Aqueous Solution.** OCTAVE BAILLY (*Compt. rend.*, 1920, 170, 1061—1064).—Methyl sulphate reacts with an aqueous solution of trisodium phosphate to give 77.8% of disodium methyl phosphate and 6.2% of sodium dimethyl phosphate, the former being converted into its barium salt, which may readily be isolated. With ethyl sulphate, the yield of the monoethyl phosphate is much lower and of the diethyl phosphate slightly higher. If disodium hydrogen phosphate is used in place of the trisodium salt, the total yield of the esters is lower, and sodium

dihydrogen phosphate or phosphoric acid does not react in aqueous solution with methyl or ethyl sulphate. W. G.

**The Constitution of the Glycerophosphoric Acids.** OCTAVE BAILLY (*Bull. Soc. chim. biol.*, 1919, 1, 152—162).—By decomposition of barium glycerophosphate, obtained from lecithin, with sodium carbonate in aqueous solution, a solution of sodium glycerophosphate was obtained, which was separated into two fractions, one crystalline and the other non-crystalline.

The non-crystalline fraction gave a calcium salt, which yielded on oxidation with bromine water evidence of the formation of an ether of dihydroxyacetone. This points to the calcium salt being a salt of  $\alpha$ -glycerophosphoric acid. The crystalline sodium salt appears to be a derivative of the  $\beta$ -acid. Therefore the glycerophosphoric acid obtained by the hydrolysis of lecithin is a mixture of the two isomerides. J. C. D.

**Action of Water on  $\beta\beta'$ -Dichlorodiethyl Sulphide.** CH. BOULIN and L. J. SIMON (*Compt. rend.*, 1920, 170, 845—848).— $\beta\beta'$ -Dichlorodiethyl sulphide is slowly decomposed by cold water and rapidly by boiling water, giving hydrochloric acid and dihydroxydiethyl sulphide. The reaction is an equilibrium phenomenon, and is considerably influenced by the temperature and the relative proportions of dichlorodiethyl sulphide and water used. Both acids and alkalis exert a retarding influence on the decomposition.

The solubility of dichlorodiethyl sulphide in cold water is 0.48 gram per litre. It is increased by the presence of dihydroxydiethyl sulphide. The presence of the latter in small amounts also accelerates the decomposition of dichlorodiethyl sulphide, but as its concentration increases, the velocity of decomposition decreases.

W. G.

**Sulphur Derivatives of Butyl Alcohol.** H. LEB. GRAY and GURNEY O. GUTEKUNST (*J. Amer. Chem. Soc.*, 1920, 42, 856—860).—Dibutyl sulphide is best prepared by boiling aqueous solutions of sodium butyl sulphate and sodium sulphide in a reflux apparatus, and subsequently distilling; if the mixture is distilled without previous boiling, butyl mercaptan is also produced. The method of oxidation of the sulphide to the sulphone by nitric acid, recommended by Grabowsky (1874), is untrustworthy, but excellent results are obtained by the use of sodium permanganate in neutral solution. J. K.

**Catalytic Decomposition of Fatty Acids by Carbon.** J. B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1920, 170, 1064—1067).—When acetic acid or its homologues are passed over purified animal charcoal at 360—380°, the acids are decomposed, giving a mixture of carbon dioxide, ethylenic hydrocarbons, carbon monoxide, methane and its homologues, and hydrogen, together with water and small amounts of ketones and aldehydes. With carbon from sugar, a considerably higher temperature is necessary, but the products are much the same. W. G.

**Remarkable Similarity in the Form of Crystals and Microbes.** ARMINIUS BAU (*Zeitsch. techn. Biol.*, 1919, **7**, 203—213; from *Chem. Zentr.*, 1920, i, 495).—With the aid of microphotographs (magnification, 1000 times), the author describes crystals of calcium oxalate which differ from the usual crystals in such a manner that they can easily be mistaken for *Saccharomycetes* or rod-like bacteria. The crystals are obtained by precipitation of solutions containing oxalic acid with calcium acetate, and may readily be distinguished from living matter by their ready solubility in moderately dilute hydrochloric, nitric, or sulphuric acid.

H. W.

**Preparation of Fat and Wax-like Substances.** FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 318222; from *Chem. Zentr.*, 1920, ii, 536).—Adipic acid or its derivatives or homologues is esterified with dihydroxylated hydrocarbons or their derivatives. *Glycyl adipate* is obtained as a tallow-like mass when adipyl chloride dissolved in pinacolin is treated with a solution of ethylene glycol and pyridine in the same solvent; the ester may also be prepared from ethylene dibromide and potassium adipate. *Glycyl α-methyladipate*, brown, waxy mass, is obtained from ethylene oxide and α-methyladipic acid. *Propyleneglycyl adipate*, from propylene iodide and potassium adipate, resembles butter.

H. W.

**The Supposed Methanetetra-carboxylic Acid.** EYVIND BÆDTKER (*Bull. Soc. chim.*, 1920, [iv], **27**, 257—258).—The substance previously described as methanetetra-carboxylic acid (compare A., 1916, i, 2) is now shown to be ammonium tetraoxalate.

W. G.

**Preparation of Glyoxal.** ALEXANDER BOSSHARD (Brit. Pat. 140478).—When ozone acts on acetylene in presence of a large proportion of air, oxygen, or other indifferent gas, the reaction ceases to be violent in character and results in the production of glyoxal. Proportions which have been found successful are 1—2% of ozone, 3—4% of acetylene, and 94—96% of air. The process is facilitated by the presence of water vapour or the use of a water spray, whereby the glyoxal is washed out of the gaseous mixture and separates as a concentrated solution.

G. F. M.

**Experiments on the Preparation of Oximino-derivatives.** WILLIAM KERSHAW SLATER (*T.*, 1920, **117**, 587—591).

**Glucal and its Conversion into New Substances of the Dextrose Series.** EMIL FISCHER, MAX BERGMANN, and HERBERT SCHOTTE (*Ber.*, 1920, **53**, [B], 509—547).—A further study of glucal and its derivatives (A., 1913, i, 445; 1914, i, 252) leads the authors to assign the formula



to the parent substance, for the following reasons. Glucal triacetate can be converted into *d*-glucosephenylosazone, thus showing that glucal contains the normal carbon chain present in dextrose, and also that a saturated carbon atom unattached to oxygen is not present. The transformation of glucal triacetate into *d*-arabinose by means of ozone proves the double bond to be between the first and second atoms of the carbon chain. The presence of the furan ring accounts for the colour reaction with a pine shaving and the observed individuality of one of the acetyl groups of glucal triacetate. Only three oxygen atoms of hydroglucal are present in hydroxyl groups, and the stability of the substance towards hydrochloric acid renders the presence of an ethylene or trimethylene oxide ring improbable. The location of the tetramethylene ring in the glucal molecule is deduced from the smooth conversion of glucal triacetate into a derivative of dextrose, and from the proof that the carbon atom, 6, does not participate in the formation of glucal.

Glucal triacetate is transformed by ozone in glacial acetic acid solution into *d*-arabinose triacetate and the *triacetyl* derivative of a pentanetetrotic acid (probably arabonic acid), long needles or prisms, m. p. 127° after much softening at 120°,  $[\alpha]_D^{25} + 27.23^\circ$  in alcoholic solution; the former showed little tendency to crystallise, and was therefore immediately hydrolysed to *d*-arabinose, which was identified as the *p*-bromophenylhydrazone and the phenylbenzylhydrazone, colourless, shining leaflets, m. p. 177—178° (corr.),  $[\alpha]_D^{16} + 14.4^\circ$  in methyl alcohol.

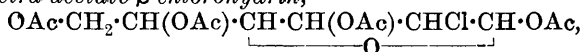
Glucal triacetate is converted into *d*-glucosephenylhydrazone by the following process. The additive product of bromine and glucal triacetate (Fischer, *loc. cit.*) is treated with silver acetate, and thus converted into a mixture of stereoisomeric *tetra-acetylglucose-β-bromohydrins*,  $\text{OAc} \cdot \text{CH}_2 \cdot \text{CH}(\text{OAc}) \cdot \text{CH} \cdot \text{CH}(\text{OAc}) \cdot \text{CHBr} \cdot \text{CH} \cdot \text{OAc}$ ,  
 $\text{O} \quad \text{O} \quad \text{O} \quad \text{O}$

which is deacetylated by dilute hydrochloric acid and then treated with phenylhydrazine; the yield is about 60%.

Glucal triacetate reacts with a saturated solution of hydrogen bromide in glacial acetic acid to yield *glucal diacetate hydrobromide*, slender needles, m. p. 99—100°; the substance exhibits mutarotation in acetylene tetrachloride, chloroform, or alcohol, but is recovered unchanged from its solutions. It contains a free hydroxyl group, since it is transformed by acetic anhydride in the presence of pyridine into *glucal triacetate hydrobromide*, prisms, m. p. 82—85°,  $[\alpha]_D^{19} + 54.43^\circ$  in tetrachloroethane, which does not show mutarotation. The constitution of these substances has not been definitely elucidated.

The addition of bromine to glucal triacetate yields a mixture of unstable dibromides, from which on some occasions it has been found possible to isolate a crystalline compound,  $\text{C}_{12}\text{H}_{16}\text{O}_7\text{Br}_2$ , m. p. 117—118° (corr.), which, however, was not optically homogeneous and the isolation of which could not be subsequently effected after loss of seeding material. The corresponding *dichloride* proved to be more stable, but in spite of homogeneous appearance and

constant, if slightly indefinite, m. p. (92—94°), it was likewise not optically uniform, and appeared to consist of a mixture of varying proportions of stereoisomerides; the most active preparation had  $[\alpha]_D^{15} + 199.7^\circ$  in tetrachloroethane solution. The dichloride is transformed by silver acetate in glacial acetic acid solution into *glucosetetra-acetate-β-chlorohydrin*,



monoclinic-sphenoidal crystals,  $a : b : c = 0.7786 : 1 : 0.7030$ ,  $\beta = 117^\circ 53\frac{1}{2}'$ , m. p. 110—111°,  $[\alpha]_D^{18} + 51.1^\circ$  in tetrachloroethane.

Crude glucal triacetate dibromide is converted by methyl alcohol and silver carbonate into a mixture of *triacetylmethylglucoside-β-bromohydrins*: (1) rhombic, bisphenoidal crystals,

$$a : b : c = 0.2602 : 1 : 0.2855,$$

m. p. 139° (corr.),  $[\alpha]_D^{18} + 50.2^\circ$  in tetrachloroethane, and (2) monoclinic, sphenoidal crystals,  $a : b : c = 2.7028 : 1 : 1.6237$ ,  $\beta = 99^\circ 52'$ , m. p. 115—116°,  $[\alpha]_D^{18} - 92.0^\circ$  in tetrachloroethane. The acetyl compounds can be deacetylated by methyl-alcoholic ammonia, and yield the corresponding *methylglucoside-β-bromohydrins*: (1) m. p. 181—182° (slight decomp.),  $[\alpha]_D^{14} + 0.87^\circ$  in aqueous solution, and (2) m. p. 182—183° (corr.; decomp.),  $[\alpha]_D^{16} - 63.8^\circ$  in aqueous solution; the former does not reduce Fehling's solution and is stable towards *N*-hydrochloric acid, whereas the latter is readily attacked. *Triacetylmethylglucoside-β-chlorohydrin*, thin prisms, m. p. 150—151° (corr.),  $[\alpha]_D^{18} + 40.0^\circ$  in tetrachloroethane, is very readily obtained from glucal triacetate dichloride, only one modification appearing to be formed. On deacetylation, it gives *methylglucoside-β-chlorohydrin*, slender needles, m. p. 164° after softening at about 159°,  $[\alpha]_D^{18} - 12.05^\circ$  in aqueous solution.

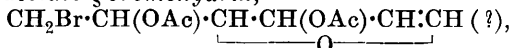
*Methyl epiglucosamine*,  $\text{OMe} \cdot \text{C}_6\text{H}_{10}\text{O}_4 \cdot \text{NH}_2$ , is obtained in the form of its salts by the action of hot aqueous ammonia on methylglucoside-β-bromohydrin (1) or methylglucoside-β-chlorohydrin; the *hydrobromide* crystallises in needles, m. p. about 215° (decomp.),  $[\alpha]_D^{20} - 123.8^\circ$  in aqueous solution, whilst the *hydrochloride* decomposes at 210—211° and has  $[\alpha]_D^{19} - 146.6^\circ$  in water. The glucoside is not attacked by emulsin or yeast extract. *Methyl epiglucosamine* could only be isolated as a syrup. *Tetra-acetylmethyl epiglucosamine* is, however, smoothly obtained when the above hydrochloride is treated with acetic anhydride and dry pyridine at the ordinary temperature; it forms rhombic-bisphenoidal crystals,  $a : b : c = 0.4279 : 1 : 0.3906$ , m. p. 188°,  $[\alpha]_D^{18} - 119.2^\circ$  in chloroform, and does not appear to be identical with the tetra-acetylmethylglucosamine described by Hamlin.

Treatment of either form of methylglucoside-β-bromohydrin with sodium amalgam and water (the chlorohydrin, however, is only extremely slowly affected) leads to the formation of *β-deoxymethylglucoside*,  $\text{OMe} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$ , which, in

the absence of seeding material, is best purified through the triacetyl derivative; the pure substance has m. p. 122—123° (corr.),

$[\alpha]_D^{17} - 48.22^\circ$  in aqueous solution. It does not reduce Fehling's solution, but is readily hydrolysed by *N*/10-hydrochloric acid, but not by yeast extract or emulsin. *Triacetyl-β-deoxymethylglucoside* forms rhombic-bisphenoidal crystals,  $a : b : c = 0.4701 : 1.0 : 0.5636$ , *m. p.* 96—97° after softening at 91°,  $[\alpha]_D^{19} - 30.31^\circ$  in tetrachloroethane solution.

*Glucal diacetate-ζ-bromohydrin*,



needles, *m. p.* 44—45°,  $[\alpha]_D^{16} - 43.03^\circ$  in tetrachloroethane, is obtained by the reduction of acetyldibromoglucose with zinc dust and acetic acid. It reduces Fehling's solution, adds bromine in chloroform solution, and gives a green coloration with a pine shaving; it does not, however, restore the colour of a magenta-sulphurous acid solution.

H. W.

**A Celloisobiose.** H. OST and R. PROSIEGEL (*Zeitsch. angew. Chem.*, 1920, **33**, 100).—A new biose has been isolated from the product of the acetylation of cellulose in presence of considerable quantities of sulphuric acid, the reaction being allowed to proceed for some days at 30°, or for some weeks at 15—20°, until crystals of the known cellobiose octoacetate begin to separate. *Celloisobiose*,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , is easily soluble in water, sparingly so in alcohol, and forms fine needles, which melt indefinitely at 165—190° with evolution of gas; in aqueous solution,  $[\alpha]_D + 23^\circ$ . It has a slightly sweet taste, and its reducing property is 99% of that of maltose. It is not hydrolysed by yeast, but readily yields dextrose when treated with hydrochloric acid. Whilst cellobiose showed signs of fermentation after five days (compare, however, Schliemann, *Diss.*, Hanover, 1910), celloisobiose gave no carbon dioxide.

J. K.

**The Viscosity of Solutions of Cellulose. I.** WILLIAM HOWIESON GIBSON. II. WILLIAM HOWIESON GIBSON [with LEO SPENCER and ROBERT MCCALL] (*T.*, 1920, **117**, 479—493).

**Digestive Hydrolyses by Mechanical Ionisation of the Water.** J. E. ABELOUS and J. ALOY (*Compt. rend.*, 1920, **170**, 1012—1014. Compare A., 1919, i, 310).—Simple shaking or bubbling of air through an aqueous solution or suspension of starch, lactose, neutral fats, or fibrin produces a partial hydrolysis, the amount increasing with rise in temperature. The addition of boiled digestive juices, such as saliva in the case of starch, or gastric juice in the case of fibrin, considerably increases the hydrolysis, although the enzymes in these juices were destroyed by the preliminary boiling.

W. G.

**The Supposed Fission of Starch by Formaldehyde.** M. JACOBY, W. VON KAUFMANN, A. LEWITE, and H. SALLINGER (*Ber.*, 1920, **53**, [B], 681—685).—A reply to Woker's recent criticisms (this vol., i, 10). The simple explanation of the supposed diastatic action of formaldehyde lies in the fact that the latter forms a loose additive compound with starch (which does not give a blue color-

ation with iodine), and also modifies the physical properties of the colloid; precipitation with alcohol, or with numerous electrolytes which behave similarly, yields unchanged starch, which under no conditions has suffered diastatic degradation. H. W.

**Some Properties of Inulin and Changes in its Physical State.** J. WOLFF and B. GESLIN (*Bull. Soc. chim. biol.*, 1920, 2, 19—23).—The hydrolysis of inulin is considered. Inulin prepared from chicory or dahlias is more soluble in water than that from other sources after it has been precipitated by alcohol. It can be converted into the less soluble form by evaporating the solution. The change is reversible, and is not fully understood.

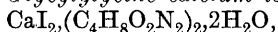
J. C. D.

**The Diastatic Hydrolysis of Inulin.** H. COLIN (*Compt. rend.*, 1920, 170, 1010—1012).—In the hydrolysis of inulin by inulase from different sources, there is no indication of the formation of any intermediate products between inulin and the reducing sugars.

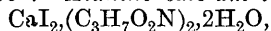
W. G.

### Preparation of Organic Derivatives of Calcium Iodide.

WALTER SPITZ (D.R.-P. 318343; from *Chem. Zentr.*, 1920, ii, 601).—Aqueous or alcoholic solutions of calcium iodide are allowed to react with neutral aqueous or alcoholic solutions of organic derivatives of ammonia, such as free or combined amino-acids or carbamides, and the additive compounds are obtained in the solid state by evaporation or spontaneous crystallisation of the solutions. *Glycine calcium iodide*,  $\text{CaI}_2 \cdot \text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \cdot 2\text{H}_2\text{O}$ , crystallises from aqueous solutions of the components in colourless, prismatic needles which decompose, without melting, above  $275^\circ$ ; the iodine is not completely precipitated by silver nitrate in nitric acid solution. *Carbamide calcium iodide*,  $\text{CaI}_2 \cdot \text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$ , obtained by boiling an aqueous solution of the components with a few drops of acetic acid under reflux, forms large, transparent plates, m. p.  $167.5^\circ$ ; the calcium is quantitatively precipitated by ammoniacal ammonium oxalate. *Glycylglycine calcium iodide*,



colourless needles, decomposes with separation of iodine, but without melting, above  $200^\circ$ . *Alanine calcium iodide*,



has m. p.  $115^\circ$ . The compounds are stable in air, not hygroscopic, and applicable in pharmacy; in contrast to calcium iodide, they are not decomposed by carbon dioxide.

H. W.

### Action of Chlorine, of Hypochlorous Acid, and of Cyanogen Chloride on Cyanamide and its Derivatives.

CH. MAUGUIN and L. J. SIMON (*Compt. rend.*, 1920, 170, 998—1001).—When chlorine is passed over cyanamide, a yellow, highly polymerised product is obtained. When the gas is passed into an aqueous solution of the amide or of calcium cyanamide, a lachrymatory product is obtained. If the solution is then warmed, a red vapour is given off, which condenses below  $0^\circ$  to a red, extremely unstable liquid,

which explodes after a few minutes. When an aqueous solution of cyanamide is added gradually to an aqueous solution of hypochlorous acid free from chlorine, and the mixture cooled to  $0^{\circ}$ , a very unstable, crystalline product, dangerous to handle, is obtained. When perfectly dry silver cyanamide is added to an excess of cyanogen chloride at  $0^{\circ}$ , a white powder is formed, which is a silver compound,  $\text{AgN}(\text{CN})_2$ , and swells up when heated. This silver compound is decomposed by hydrogen chloride in ethereal solution, giving *dicyanimide hydrochloride*,  $\text{NH}(\text{CN})_2 \cdot \text{HCl}$ , which in its turn is decomposed by water to give biuret. If the silver compound,  $\text{AgN}(\text{CN})_2$ , is decomposed in water by dilute hydrochloric acid, it gives *cyanocarbamide*,  $\text{CN} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ . W. G.

**Carbon Subnitride. Action of Halogens, of the Hydrohalogen Acids, and of Alcohols.** CHARLES MOUREU and JACQUES CH. BONGRAND (*Compt. rend.*, 1920, **170**, 1025—1028. Compare A., 1914, i, 671).—The heat of combustion of carbon subnitride agrees with the equation  $4\text{C}_{\text{diamond}} + \text{N}_{2\text{gas}} = \text{C}_4\text{N}_{2\text{solid}} - 138.3 \text{ cal.}$  The subnitride fixes all the halogens. With an aqueous solution of hydrobromic acid, the product is  *$\alpha$ -bromo- $\alpha\beta$ -dicyanoethylene*,  $\text{CN} \cdot \text{CH} \cdot \text{CBr} \cdot \text{CN}$ ,

m. p.  $48.5\text{--}49^{\circ}$ . Similarly, the subnitride adds on the elements of hydrogen iodide, giving  *$\alpha$ -iodo- $\alpha\beta$ -dicyanoethylene*, m. p.  $86\text{--}87^{\circ}$ . With hydrochloric acid, partial hydrolysis also occurs, and the product is *chloro- $\beta$ -cyanoacrylamide*, m. p.  $167^{\circ}$ , the chlorine probably being attached to the  $\alpha$ -carbon atom. When carbon subnitride is treated with absolute alcohol, it yields  *$\alpha$ -ethoxy- $\alpha\beta$ -dicyanoethylene*, m. p.  $30.5\text{--}31^{\circ}$ ,  $D_{20}^{25} 1.0166$ ,  $n_D^{25} 1.4677$ . Similar additive products are obtained with other alcohols. W. G.

**Preparation of Cyanogen Chloride on a Large Laboratory Scale.** T. SLATER PRICE and STANLEY J. GREEN (*J. Soc. Chem. Ind.*, 1920, **39**, 98T—101T).—The most convenient method for the preparation of cyanogen chloride on a large laboratory scale is by the action of chlorine on a dilute solution (12—15%) of hydrocyanic acid. The chlorine is forced into the solution through a porous pot, and the fine bubbles so produced bring about rapid chlorination. The heat of reaction is sufficient to distil over the cyanogen chloride into cooled receivers; the crude product contains water and hydrogen cyanide, together with traces of hydrochloric acid; methods of purification are described.

Instead of using a pure solution of hydrocyanic acid, the acid may be made in situ by the interaction of sodium cyanide and sulphuric acid solutions, the hydrocyanic acid solution thus produced being about 6% strength. On a large scale, this method suffers from the disadvantage that considerable cooling is necessary during the preparation of the solution of hydrocyanic acid.

The method described by Jennings and Scott (A., 1919, i, 526) is not practicable on a large scale, owing to the difficulty of regulating the temperature.

It is shown that the reaction between chlorine and hydrocyanic



acid proceeds quantitatively according to the equation  $\text{Cl}_2 + \text{HCN} = \text{CNCl} + \text{HCl}$ .

Pure cyanogen chloride has b. p.  $13^\circ$  (uncorr.) and m. p.  $-8^\circ$ ,  $D_4^{20}$  1.207, and  $D_4^{25}$  1.218. By the action of hydrogen chloride, the following effects are produced: (a) The cyanogen chloride is polymerised to cyanuric chloride, the reaction taking place slowly and only to any extent in the absence of water. (b) Hydroxylation of the cyanogen chloride to cyanic acid and carbon dioxide, and hence to ammonium chloride and carbon dioxide. This is a much more rapid reaction than (a), the velocity increasing with the strength of the acid. The action is complete in a few hours with 9*N*-HCl; with 2*N*-acid, the reaction is very slow, and even with 5*N*-acid takes several days. The pure substance does not undergo polymerisation, and dry chlorine and carbonyl chloride have no action on it.

In an addendum, a small-scale continuously acting apparatus is described.

T. S. P.

**Methylstannonic Acid and some of its Salts and Derivatives.** J. G. F. DRUCE (*Chem. News*, 1920, 120, 229—230).—

In view of the suggestion that potassium hydrogen stannite has a structure similar to that of potassium formate (Hantzsch, A., 1902, ii, 289), the relationship of methylstannonic acid to acetic acid has been studied, but they are found to have little in common. The corresponding methylstannonates are precipitated on the addition of copper, zinc, nickel, or ferrous sulphates to solutions of the alkali salts. The acid is insoluble in solutions of the alkaline carbonates or in organic solvents, but soluble in mineral acids, acetic and tartaric acids. It is infusible, but when strongly heated is decomposed into stannic oxide, methane being also produced in absence of air. Stannic oxide is also produced when the acid is gently heated with ammonium nitrate. A modification of Pfeiffer and Lehnardt's method of preparing the acid (A., 1903, i, 470, 802) consists in the careful acidification of the residual solution after removal of alcohol at  $40^\circ$  from the product of the action of methyl iodide on an alcoholic potassium stannite solution at the ordinary temperature for three days. Methylstannoyl potassium carbonate, which is produced by Pfeiffer's process, forms crystalline platelets, the solution of which in water is alkaline in reaction and suffers decomposition either by heat or by dilute hydrochloric acid, carbon dioxide being produced in the latter case. *Aniline methylstannichloride*,  $(\text{NH}_2\text{Ph})_2\text{H}_2\text{MeSnCl}_5$ , prisms, m. p.  $214^\circ$ , from tin methyl chloride or methylstannonic acid and aniline hydrochloride, forms an acid solution, unaltered by boiling. *Methyl-aniline methylstannichloride*,  $(\text{NHMePh})_2\text{H}_2\text{MeSnCl}_5$ , granules, m. p.  $194^\circ$ . *Pyridine methylstannichloride*,  $\text{Py}_2\text{H}_2\text{MeSnCl}_5$ , yellow plates, m. p.  $300^\circ$ .

J. K.

**Catalytic Oxidation. I. Benzene.** JOHN MORRIS WEISS and CHARLES R. DOWNS (*J. Ind. Eng. Chem.*, 1920, 12, 228—232. Compare this vol., i, 216, 236).—An outline of investigations of

the catalytic oxidation of benzene, especially the formation of maleic acid. In this reaction, using vanadium dioxide as catalyst, temperature control is the most important factor. The apparatus employed consisted essentially of a vaporiser and mixer, a contact tube, and a condensing system; the contact tube was immersed in a metal bath kept at a definite temperature. W. P. S.

**The Introduction of the Chloromethyl Group into the Aromatic Nucleus.** HENRY STEPHEN, WALLACE FRANK SHORT, and GEOFFREY GLADDING (T., 1920, 117, 510—527).

**[Freezing Points of Binary and Ternary Systems of Nitrotoluenes.]** E. CHABANIER (*Mon. Sci.*, 1920, [v], 10, 80).—The method of determining the freezing points of component systems of nitrotoluenes described by Bell and Herty (this vol., i, 152) is the most trustworthy yet devised; but to obtain concordant results, the supercooling must not be too pronounced, since the temperature does not subsequently rise to the same extent as when there is only slight supercooling. Owing to the variable influence of supercooling, the melting-point curves thus obtained will be slightly below the true curves for binary systems. Applying the hypothesis of Bell and Herty, the eutectic points of binary mixtures of 2:3-, 2:4-, 2:5-, and 2:6-dinitrotoluenes have been calculated. The method is also applicable to the study of nitration processes. For example, direct nitration of toluene to dinitrotoluene gives mixtures of 2:4- and 2:6-dinitrotoluene, from which crystals solidifying at 66—67° can be separated, whereas by the nitration of mononitrotoluene to dinitrotoluene, a mixture solidifying at about 59° is obtained. In like manner, differences may be observed in the products obtained by nitrating toluene to trinitrotoluene directly or in three stages. C. A. M.

**The Electrochemical Oxidation of *p*-Nitrotoluene and of its Isomerides.** FR. FICHTER and GÉRALD BONHÔTE (*Helv. Chim. Acta*, 1920, 3, 395—409).—Contrary to the statement of Elbs that the electrochemical oxidation of *p*-nitrotoluene does not proceed beyond the formation of *p*-nitrobenzyl alcohol (A., 1897, i, 332), it is shown that under varying conditions in acetic-sulphuric acid solution with a platinum anode, both *p*-nitrobenzaldehyde and *p*-nitrobenzoic acid are produced (compare Coehn, *Zeitsch. Elektrochem.*, 1903, 9, 643; Labhardt and Zschoche, A., 1902, i, 289). The alcohol owes its protection from further oxidation to the simultaneous formation of a tarry product, of low nitrogen content and phenolic in character, together with nitric acid as a result of the replacement of the nitro-group of *p*-nitrotoluene by hydroxyl. In virtue of its easy oxidisability (compare A., 1914, i, 946), this product acts as a depolariser. The acetic acid also plays a part by protecting the alcohol from the action of the nitric acid; if aqueous sulphuric acid be used, a better yield of *p*-nitrobenzoic acid is produced, and *p*-nitrobenzyl alcohol can only be isolated with difficulty. Experiments on the electrolytic oxidation

of phenol showed that the formation of carbon dioxide was greatly increased by nitric acid, but this effect was negligible when acetic acid was also present. Successively better yields of *p*-nitrobenzoic acid, without the formation of tar, are obtained by replacing *p*-nitrotoluene by *p*-nitrobenzyl alcohol or *p*-nitrobenzaldehyde, whether acetic acid be present or not. Owing to its greater oxidisability, *o*-nitrotoluene suffers complete decomposition in aqueous sulphuric acid, but in acetic-sulphuric acid gives a smaller yield of nitrobenzyl alcohol than the para-isomeride (compare Pierron, A., 1901, i, 685), with some tar, whilst the alcohol and the aldehyde may be respectively oxidised in good yield to the aldehyde and the acid. By oxidation in presence of dilute sulphuric acid, *m*-nitrotoluene also suffers complete decomposition, but *m*-nitrobenzyl alcohol cannot be detected among its oxidation products in acetic-sulphuric acid solution, since, like toluene, it yields the aldehyde, or, with sufficient current density, the acid. This may also easily be obtained in good yield from the alcohol and the aldehyde. In explanation of this difference from the ortho- and para-isomerides, it is shown that, of the series *p*-nitrotoluene, *p*-nitrobenzyl alcohol, *p*-nitrobenzaldehyde, and *p*-nitrobenzoic acid, the alcohol shows the maximum polarisation value in presence both of aqueous- and of acetic-sulphuric acids, and, in consequence, it is suggested that a peroxide of *p*-nitrobenzyl alcohol is formed which increases the oxidising effect of the anode on the higher oxidation products. If platinum be replaced by lead peroxide as anode, the alcohol is no longer obtained. When the alcohol is used as starting material, it reacts with any peroxide to form the aldehyde, and so weakens its protective action. The polarisation values of *o*- and *m*-nitrobenzyl alcohols are very small, in accordance with the smaller yields obtained of these substances.

J. K.

**Formation and Decomposition of Aromatic Sulphonic Acids by Electrochemical Oxidation.** FR. FICHTER, ROBERT BRÄNDLIN, and ERNST R. HALLAUER (*Helv. Chim. Acta*, 1920, **3**, 410—422. Compare A., 1914, i, 811).—By electrolytic oxidation of ammonium 4:4'-disulphodiphenyl disulphide at a platinum anode, benzene-*p*-disulphonic acid is produced in 88% yield, but is only freed with difficulty from impurities, presumed to arise from its oxidation (compare Tonoli, *Chem. Zeit.*, 1912, **36**, 939). Experiments on the electrolytic oxidation of ammonium benzene-*p*-disulphonate itself indicated the formation of a phenolic compound as intermediate product, the final product being isolated as a *barium* salt, to which the formula  $C_{12}H_4O_{16}S_3Ba_4$  is assigned with reserve. Phenol-2:5-disulphonic acid is probably an intermediate product, since on oxidation it exhibits a similar series of colour changes, probably involving the formation of catechol-4-sulphonic acid. Benzene-*m*-disulphonic acid also appears to furnish phenolic compounds (possibly catechol-4-sulphonic acid and quinolsulphonic acid), since the odour of *p*-benzoquinone is observed and the solution gives a green coloration with ferric chloride, but suffers com-

plete decomposition without offering the possibility of isolating intermediate products. J. K.

**Purification of Decahydronaphthalene** TETRALIN G.M.B.H. (D.R.-P. 310781; from *Chem. Zentr.*, 1920, ii, 601—602).—Incompletely hydrogenated naphthalene is treated with liquid sulphur dioxide; naphthalene and its tetra-, hexa-, and octa-hydrated derivatives readily pass into solution, whilst decahydronaphthalene is practically insoluble in this medium. H. W.

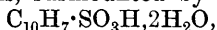
**Preparation of Chlorinated Nitronaphthalenes.** OSKAR MATTER (D.R.-P. 317755; from *Chem. Zentr.*, 1920, ii, 601).—The chloro-additive compounds of naphthalene are treated with nitric acid at a low temperature, and the products so formed are heated with water or with reagents which combine with acids. Thus, naphthalene dichloride and nitric acid (D 1.5) yield a *nitronaphthalene dichloride* which, when boiled with water or heated with milk of lime, passes into 8-chloro- $\alpha$ -nitronaphthalene, m. p. 93—94°; the latter is reduced by stannous chloride and hydrochloric acid to 8-chloro- $\alpha$ -naphthylamine, m. p. 88—89°. Similarly, naphthalene tetrachloride and nitric acid (D 1.5) form a resinous *nitronaphthalene tetrachloride*, which is transformed by methyl alcohol and sodium carbonate, or by benzene, methyl alcohol, and sodium hydrogen carbonate at 140—150°, into 5:8-dichloro- $\alpha$ -nitronaphthalene, m. p. 94°. 5:8-Dichloro- $\alpha$ -naphthylamine, m. p. 104—105°, is prepared by reducing the latter with tin and hydrochloric acid. H. W.

**The Reduction of Nitronaphthalenesulphonic Acids.** HANS EDUARD FIERZ and PAUL WEISSENBACH (*Helv. Chim. Acta*, 1920, 3, 305—311).—The results of previous investigators have tended to show complete agreement between the nitro-derivatives of benzene and of naphthalene in their behaviour on reduction. It is now found that the reduction, whether electrolytic or by means of iron and ferrous sulphate, of 5-nitro- and 8-nitronaphthalene-2-sulphonic acid only yields the corresponding hydroxylamines (compare D.R.-P. 81621). The resulting solutions have strong reducing properties, and give red precipitates of unstable Schiff's bases when treated with formaldehyde and dimethylaniline. Complete reduction is only achieved in weakly acid solution, for example, by the use of ferrous acetate. The 5- and 8-nitronaphthalene-1-sulphonic acids, however, and also 8-nitronaphthalene-1:3:6-trisulphonic acid, may be reduced electrolytically to the amino-acids in 10% sulphuric acid solution, a current density of 200—600 amp./dm.<sup>2</sup> being employed between lead electrodes.

The dissociation constants of the following acids are given: naphthalene-1-sulphonic acid, 0.18; naphthalene-2-sulphonic acid, 0.25 (compare Wegscheider and Lux, A., 1909, ii, 649); 5-nitronaphthalene-1-sulphonic acid, 0.15, the 8-nitro-isomeride, 0.094;

5-nitronaphthalene-2-sulphonic acid, 0·10, the 8-nitro-isomeride, 0·13; 8-nitronaphthalene-1:3:6-trisulphonic acid, 0·055. J. K.

**Naphthalene-1-sulphonic Acid.** HANS EDUARD FIERZ and PAUL WEISSENBACH (*Helv. Chim. Acta*, 1920, **3**, 312—318).—It is shown that the sulphonation of naphthalene, even at low temperatures, always results in the formation of some naphthalene-2-sulphonic acid, for example, at least 2% at 0° (Euwes, A., 1909, i, 707). The determination of the proportion is based on the fact that the 1-acid crystallises from aqueous solution as a dihydrate, whilst the 2-acid forms a trihydrate. Apparently the process of sulphonation consists in the formation of a molecular compound, which undergoes decomposition into either the 1- or the 2-acid, according to the prevailing external conditions. Naphthalene-1-sulphonic acid separates from aqueous solution in the form of tiny, non-deliquescent columns, surmounted by pyramids,



m. p. 90°, which cannot be completely dehydrated without decomposition. The *ammonium* salt,  $\text{C}_{10}\text{H}_7\cdot\text{SO}_3\cdot\text{NH}_4$ , pearly leaflets; the *lead* salt,  $(\text{C}_{10}\text{H}_7\text{SO}_3)_2\text{Pb}\cdot 3\text{H}_2\text{O}$ , lustrous leaflets, is converted into the monohydrate at 85°; the *zinc* salt ( $6\text{H}_2\text{O}$ ), thin leaflets; the *cobalt* salt ( $6\text{H}_2\text{O}$ ), lustrous, pale red leaflets, is bluish-violet when anhydrous; the *nickel* salt ( $6\text{H}_2\text{O}$ ), lustrous, light green leaflets, turns yellow and becomes anhydrous at 185°; the *copper* salt ( $6\text{H}_2\text{O}$ ), turquoise-blue leaflets, is dehydrated and turned yellow at 180°; the *cadmium* salt ( $6\text{H}_2\text{O}$ ) and the *zinc* salt ( $6\text{H}_2\text{O}$ ) form leaflets. The strontium salt crystallises as a dihydrate. J. K.

**Action of Aqueous Sodium Hydroxide on the  $\alpha$ -Naphthylaminesulphonic Acids.** HANS EDUARD FIERZ (*Helv. Chim. Acta*, 1920, **3**, 318—329).—Diagrams of curves are given expressing the tabulated results of a quantitative study of the proportions of the products obtained by the treatment of the  $\alpha$ -naphthylamine-sulphonic acids with varying strengths of sodium hydroxide solution at different temperatures. The following products are obtained, the figures in brackets indicating the maximum proportion observed, with the corresponding temperature and strength of alkali employed, time of action in all cases being three hours; from  $\alpha$ -naphthylamine-4-sulphonic acid:  $\alpha$ -naphthol (59%),  $\alpha$ -naphthol-4-sulphonic acid (54%; 280°, 10%), 1:4-dihydroxynaphthalene (traces), but no  $\alpha$ -naphthylamine; from  $\alpha$ -naphthylamine-5-sulphonic acid, 1:5-dihydroxynaphthalene (60·2%; 290°, 30 or 50%), 5-amino- $\alpha$ -naphthol (52·4%; 250°, 30%),  $\alpha$ -naphthylamine (7·8%; 300°, 50%), and probably a little  $\alpha$ -naphthol-5-sulphonic acid; from  $\alpha$ -naphthylamine-6-sulphonic acid,  $\alpha$ -naphthol-5(?) -sulphonic acid (49%; 260°, 20%), 1:6-dihydroxynaphthalene (17%; 260°, 50%),  $\alpha$ -naphthylamine (0·3%; 260°, 20 or 50%), unchanged acid (37%; 260°, 20%) and traces of 5-amino- $\beta$ -naphthol; from  $\alpha$ -naphthylamine-7-sulphonic acid,  $\alpha$ -naphthol-7-sulphonic acid (40%[?]; 260°, 50%), 8-amino- $\beta$ -naphthol (37·7%; 260°, 50%), 1:7-dihydroxynaphthalene (3%; 260°, 20%), unchanged acid (55%;

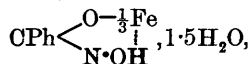
260°. 20%); from  $\alpha$ -naphthylamine-8-sulphonic acid, 1:8-dihydroxy-naphthalene (46.6% [70% by very rapid heating]; 300°, 10%),  $\alpha$ -naphthylamine (32.5%),  $\alpha$ -naphthol-8-sulphonic acid, and traces of 8-amino- $\alpha$ -naphthol. Some naphthalene is always produced when naphthalene-1- or -2-sulphonic acids are fused with sodium hydroxide solution (compare Willson and Meyer, A., 1915, i, 232).

J. K.

**Preparation of Hexanitrodiphenylamine and its Use as a Primer in Shell Charges.** JOHN MARSHALL (*J. Ind. Eng. Chem.*, 1920, **12**, 336—340).—Hexanitrodiphenylamine is more stable than tetranitromethylaniline or tetranitroaniline, and is superior to trinitrotoluene as a detonator. It may be prepared on a large scale by a modification of Carter's method (*Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1913, 205) of nitrating aniline. In the first stage, two mols. of aniline and one mol. of chloronitrobenzene are emulsified with hot water, and the temperature raised to 80° for an hour. Dinitrodiphenylamine is precipitated in clusters of red needles melting at 148° to 152°. This is converted into tetranitrodiphenylamine by nitration with a suitable mixture of nitric and sulphuric acids, first at 70° and then at 80° to 90°, yielding a brownish-yellow, amorphous mass containing small amounts of higher nitration products. The final nitration of this material is effected at 90°, and yields up to 80% of the theoretical amount of hexanitrodiphenylamine in yellow crystals melting at 238.5—239.5°. The method of nitrating dinitrodiphenylamine in one operation, suggested by Hoffmann and Dame (A., 1919, i, 394), is less suitable, since it yields an amorphous material melting at 238°. The absolute density of the crystalline product was 1.653. [See, further, *J. Soc. Chem. Ind.*, 1920, 429A.] C. A. M.

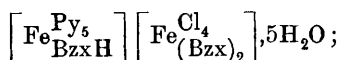
**Preparation of Diarylurethanes.** CHEMISCHE FABRIKEN VORM WEILER TER MEER (D.R.-P. 306316; from *Chem. Zentr.*, 1920, ii, 491—492).—The diarylamine or its hydrochloride (one molecule) is warmed with one or more molecules of ethyl chloroformate in the presence or absence of a solvent until hydrogen chloride ceases to be evolved. When only one molecule of diarylamine is employed, a quantitative conversion of diarylamine into urethane is effected, and free hydrogen chloride is evolved. The preparation of diphenylurethane from diphenylamine and chloroformic ester is particularly described. H. W.

**Ferribenzhydroxamic Acid Compounds.** R. F. WEINLAND and GERTRUD BAIER (*Ber.*, 1920, **53**, [B], 685—696).—Addition of aqueous ferric chloride to a solution of sodium benzhydroxamate in water yields the sparingly soluble ferribenzhydroxamate,



reddish-brown rods or six-sided platelets from 96% alcohol, needles from more dilute alcohol. The substance behaves as an internally

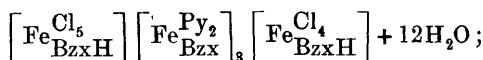
complex salt; it dissolves readily in aqueous solutions of all types of bases and in dilute acids, apparently with formation of salts, which can only exist in solution, since the latter ultimately deposits the original material. From alcoholic solutions of ferric chloride, benzhydroxamic acid and pyridine (or quinoline), the following series of *salts* has been prepared [in the formulation of which BzxH represents the benzhydroxamic acid molecule and Bzx the radicle  $\text{PhC}(\text{:N}\cdot\text{OH})\cdot\text{O}$ ]: (i) rectangular, violet platelets,



(ii) pale violet, irregular, six-sided platelets,  $\left[ \text{Fe}_{\text{Bzx}}^{\text{Py}_5} \right] \left[ \text{Fe}_{\text{Py}}^{\text{Cl}_4 \text{ Bzx}} \right]$ ,

which are converted by water into ferribenzhydroxamate; (iii) the cherry-red salts  $\text{FeCl}_3\cdot\text{BzxHPy}$  and  $\text{FeCl}_3\cdot\text{BzxH Quinoline}$ , which are soluble in water and are to be regarded simply as the pyridine and quinoline salts of a trichlorobenzhydroxamatoferri-acid,

$\left[ \text{Fe}_{\text{Bzx}}^{\text{Cl}_3} \right] \text{H}$ ; (iv) dark red, shining powder,



(v) dark red salt,  $\left[ \text{FeCl}_5 \right] \left[ \text{Fe}_{\text{Bzx}_2}^{\text{Quinoline}_2} \right]_3 \left[ \text{Fe}_{\text{BzxH}}^{\text{Cl}_4} \right] + 6\text{H}_2\text{O};$

(vi) reddish-brown needles,  $2 \left[ \text{Fe}_{\text{Bzx}_2}^{\text{Py}} \right] \left[ \text{Fe}_{\text{Bzx}_3}^{\text{Py}} \right] + 6\text{H}_2\text{O}$ . The

preparation of the individual salts is effected by suitably varying the relative proportions of the components; for details, the original must be consulted. H. W.

**Preparation of Dinitrophenol.** OSWALD SILBERRAD (Brit. Pat. 140955).—2:4-Dinitrophenol is obtained by suspending 100 parts of *p*-nitrosophenol in a solution of 200 parts of sodium nitrate in 350 parts of water and running the mixture into 480 parts of 50% sulphuric acid at 70–80°, the temperature being finally raised to, and maintained for six hours at, 95°. The yield amounts to 135 parts of dinitrophenol, representing 130% on the phenol initially employed. If desired, nitric acid (D 1.2) may be substituted for the sodium nitrate and sulphuric acid. G. F. M.

**Preparation of Pyrogallol.** NITRITFABRIK AKT.-GES. (Brit. Pat. 140694).—Pyrogallol is obtained in nearly theoretical yield by heating solutions or suspensions of tannic or gallic acids at temperatures above 160° in an autoclave, with a proportion of alkali or alkaline earth, etc., hydroxides or carbonates not materially exceeding twice the amount required to effect substitution of the hydrogen atoms of the carboxyl groups initially present and those formed by hydrolysis, if any. G. F. M.

**The Valency Problem of Sulphur. III.** H. LECHER (*Ber.*, 1920, **53**, [B], 577—590. Compare A., 1915, i, 532; 1916, i, 41).—In previous communications (A., 1915, i, 532; 1916, i, 41), evidence has been brought forward to show that diphenyl disulphide and di-*p*-dimethylaminodiphenyl disulphide are not appreciably dissociated into free radicles, since their solutions obey Beer's law. This method of attacking the problem is not, however, sufficiently accurate to enable conclusions to be drawn as to the possibility of a slight dissociation. A different mode of working has now been adopted, and it is shown that a solution of molar amounts of diphenyl disulphide and di-*o*-nitrodiphenyl disulphide in boiling xylene is unchanged after three hours, and in benzene at 200° is unaltered after six hours, and that the same is true of equivalent solutions of *o*-nitrodiphenyl disulphide in the same solvents. From these experiments, the conclusion is drawn that the solutions of the latter substance cannot contain any free radicle, and, whilst a partial dissociation of one of the symmetrical disulphides is not absolutely excluded, it is highly improbable that such is actually the case.

Diphenyl disulphide, di-*p*-dimethylaminodiphenyl disulphide, di-*o*-nitrodiphenyl disulphide, and *o*-nitrodiphenyl disulphide exhibit thermochromic properties, darkening when heated in the crystalline or molten condition or when in solution, and returning to their original colour when cooled. The phenomenon is exhibited most strongly by the dimethylamino-, least strongly by the nitro-derivatives. It does not appear to depend on the formation of free radicles, and is not a specific property of the disulphide group, since it is also exhibited by *o*-nitrodiphenyl sulphide. It may possibly be partly attributable to the presence of the nitro-group, since nitrobenzene is itself thermochromic.

The dissociation of mercury phenylmercaptide into mercury and diphenyl disulphide,  $\text{Hg}(\text{SPh})_2 = \text{Hg} + \text{PhS} \cdot \text{SPh}$ , does not appear to be attributable to a preliminary detachment of the SPh-radicle, since *o*-nitrodiphenyl disulphide is found to react with mercury under conditions which preclude the presence of the free radicle; the products of the action are diphenyl disulphide, di-*o*-nitrodiphenyl disulphide, and *mercury o-nitrophenylmercaptide*, small, yellow, very electric needles, m. p. 231° (decomp.) after softening at 222° and darkening at 228°.

*o*-Nitrodiphenyl disulphide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{SPh}$ , long, yellow crystals, m. p. 55°, is smoothly prepared by the action of *o*-nitrochloroethiolbenzene (Zincke and Farr, A., 1912, i, 763) on phenylmercaptan in dry ethereal solution.

H. W.

### Reduction of Organic Disulphides by Alkali Mercaptides.

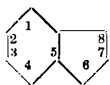
H. LECHER (*Ber.*, 1920, **53**, [B], 591—593).—The author has attempted to prepare *o*-nitrodiphenyl disulphide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{SPh}$ , by the action of *o*-nitrochloroethiolbenzene (Zincke and Farr, A., 1912, i, 763) on sodium phenyl sulphide, but has thereby obtained



mainly a mixture of the *s*-diphenyl disulphide and di-*o*-nitrodiphenyl disulphide. The *as*-disulphide is shown to be formed primarily and to be immediately reduced by the sodium phenyl sulphide to diphenyl disulphide and sodium *o*-nitrophenyl mercaptide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{SPh} + \text{PhSNa} = \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SNa} + \text{PhS} \cdot \text{SPh}$ ; the latter then reacts with *o*-nitrochlorothiobenzene to yield di-*o*-nitrodiphenyl disulphide.

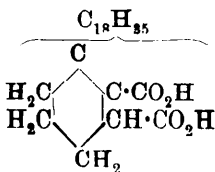
H. W.

**Cholesterol. XXIX. Certain Derivatives of Cholestene and  $\psi$ -Cholestene and the Proof of the Existence of a Methylene Group adjacent to a Double Bond in Cholesterol.** A. WINDAUS (*Ber.*, 1920, **53**, [B], 488—497).—Cholestene and  $\psi$ -cholestene have been converted into three different monoketones, in which the carbonyl group is in the positions 6, 7, and 8 respectively when the numbering shown in the annexed scheme is adopted.



Nitrocholestene, leaflets, m. p. 117—118° (Mauthner and Suida give m. p. 105°), is prepared in 75% yield by the action of fuming nitric acid (D 1.52) on a solution of cholestene in glacial acetic acid, and is converted by potassium cyanide into *nitrocholestene hydrocyanide*, long needles, m. p. 162°, from which cholestan-7-one, m. p. 98—99°, is prepared, which is identical with heterocholestanone described by Windaus and Dalmer (A., 1919, i, 204). The latter, when oxidised by chromic acid in hot glacial acetic acid solution, yields an acid product which shows no tendency to crystallise, but which, on distillation under diminished pressure, gives an unsaturated hydrocarbon,  $\text{C}_{25}\text{H}_{42}$  or  $\text{C}_{25}\text{H}_{44}$  [identical with the product obtained by Windaus and Resan (A., 1914, i, 682) by the oxidation of cholestene with permanganate], transformable by catalytic hydrogenation into a saturated hydrocarbon, m. p. 45° (see later). Similarly, 4-chlorocholestane-7-one is converted by chromic acid into a non-crystalline acid, from which an unsaturated hydrocarbon,  $\text{C}_{25}\text{H}_{40}$  or  $\text{C}_{25}\text{H}_{42}$ , m. p. 76°, is obtained, identical with the product isolated by Windaus and Resan (*loc. cit.*) by the distillation of the acidic oxidation compounds of cholesteryl acetate. Catalytic hydrogenation in ethereal solution converts the latter mainly into a saturated hydrocarbon, m. p. 80°, whilst in glacial acetic acid solution the hydrocarbon, m. p. 45° (see above), is formed.

*Nitro- $\psi$ -cholestene*,  $\text{C}_{27}\text{H}_{45}\text{O}_2\text{N}$ , has m. p. 70°, and is converted by zinc dust and acetic acid into *cholestan-6-one*, m. p. 98—99° (*oxime*, slender needles, m. p. 205°). The latter is reduced by amalgamated zinc and hydrochloric acid to cholestane, m. p. 79—80°, and is oxidised by fuming nitric acid to a dicarboxylic acid (annexed formula), m. p. 240°.



The oxidation of cholestene by a considerable excess of chromic acid in glacial acetic acid solution leads to the production of small

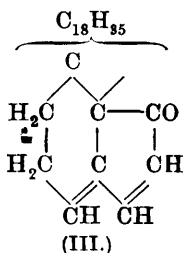
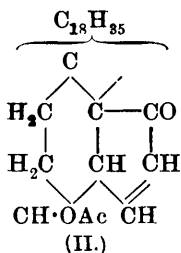
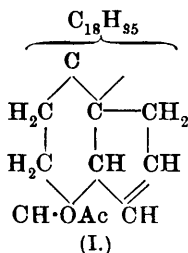
amounts (ca. 10%) of the unsaturated ketone, *ketocholestene* (annexed formula), plate-like crystals, m. p.  $145^{\circ}$  (*semicarbazone*, small needles, m. p.  $225^{\circ}$  [decomp.]). The constitution of the latter follows from its catalytic hydrogenation to *cholestane-8-one*, m. p.  $108-109^{\circ}$ , which is found to differ from either *cholestane-6-* or *-7-one*, but to be oxidised by fuming nitric acid to a dicarboxylic acid,  $C_{27}H_{46}O_4$ , identical with that obtained from *cholestane-7-one*, thus showing the keto-group to be present in the position 8. Hence, *cholestene* must contain the methylene group in juxtaposition to the group  $-CH:CH-$ , and this arrangement must also be present in the cholesterol molecule.

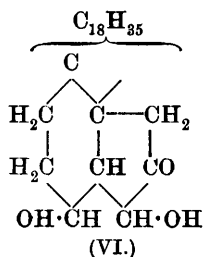
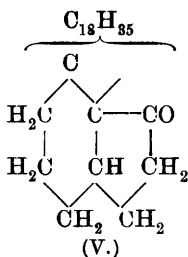
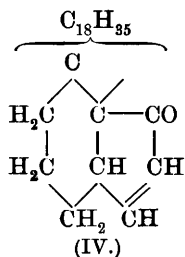
H. W.

### Cholesterol. XXX. Oxidation of Cholesteryl Acetate. A.

WINDAUS and E. KIRCHNER (*Ber.*, 1920, **53**, [B], 614—621).—The oxidation of cholesteryl acetate (I) with chromic acid (Mauthner and Suida, A., 1897, i, 31; Windaus and Resau, A., 1915, i, 677) yields a mixture of  $\beta$ -oxycholestenyl acetate and a substance,  $C_{26}H_{48}O_4$ , the constitutions of which have not been satisfactorily elucidated. Attempts have been made in this direction by Windaus and Resau (*loc. cit.*), but their arguments are based on a formula for cholesterol since disproved. Revision of the latter (preceding abstract) has enabled the problem to be solved.

$\beta$ -Oxycholestenyl acetate (II) is readily hydrolysed to the simply unsaturated keto-alcohol oxycholestenol, which readily loses water and yields the doubly unsaturated ketone, *ketocholesterylene* (III). The latter, when submitted to step-wise catalytic hydrogenation, first absorbs two atoms of hydrogen, and gives the previously described *ketocholestene* (IV), and then reacts with a further two atoms to yield *cholestane-8-one* (V) (*loc. cit.*). The same product is ultimately obtained when  $\psi$ -cholesterol (obtained from *ketocholesterylene* by means of sodium and alcohol) is first oxidised to the unsaturated ketone,  $\psi$ -cholestenone, and then catalytically hydrogenated. The oxidation of cholesteryl acetate is therefore precisely analogous to that of *cholestene*, the methylene group adjacent to the double bond being converted into the keto-group. The individual products are therefore formulated in the following manner:





It is further shown that  $\beta$ -oxycholestenyl acetate can be reduced by hydrogen in the presence of spongy palladium to *ketocholestanyl acetate*, needles, m. p. 142—143°, which, on hydrolysis, yields *cholestane-8-one-4-ol*, pearly leaflets, m. p. 156—157°; the latter is oxidised by chromic acid in the presence of acetic acid to *cholestane-4 : 8-dione*, needles, m. p. 186—187°, the *dioxime* of which has m. p. 281° (decomp.).

The substance,  $\text{C}_{29}\text{H}_{48}\text{O}_4$ , is the monoacetyl derivative of a cholestane-one-diol, which is now shown to be *isocholestane-7-one-4 : 5-diol* (VI), since, when cautiously oxidised, it passes into the previously described *isocholestane-4 : 7-dione-6-ol*, which is successively convertible into *cholestene-4 : 7-dione* and *cholestane-4 : 7-dione*.  
H. W.

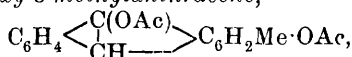
**Syntheses with the Aid of Monochloromethyl Ether. IV. The Condensation of Ethyl Benzylsodiummalonate and Monochloromethyl Ether.** JOHN LIONEL SIMONSEN (T., 1920, 117, 564—569).

**The Preparation of *cyclo*Heptane-1 : 1-diacetic Acid.** JAMES NELSON EDMUND DAY, GEORGE ARMAND ROBERT KON, and ARNOLD STEVENSON (T., 1920, 117, 639—646).

**Derivatives of  $\alpha$ -Arylphthalides and their Conversion into Anthracene Derivatives.** A. BISTRZYCKI and S. ZEN-RUFFINEN (*Helv. Chim. Acta*, 1920, 3, 369—391. Compare A., 1899, i, 151).

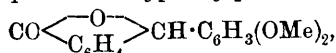
—6-Hydroxy-*m*-tolylphthalide,  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{CH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OH}$ , m. p. 164·5—165·5° (Winkler, *Diss.*, Freiburg [Switzerland], 1901), is best prepared by the condensation of *o*-phthalaldehydic acid with *o*-cresol in presence of 73% sulphuric acid; it yields a *benzoyl* derivative,  $\text{C}_{22}\text{H}_{16}\text{O}_4$ , m. p. 123—124°; ethylation gives its *ethyl ether*,  $\text{C}_{17}\text{H}_{16}\text{O}_3$ , m. p. 96·5—97·5°; its *methyl ether*,  $\text{C}_{16}\text{H}_{14}\text{O}_3$ , m. p. 124·5—125·5°, is formed from *o*-phthalaldehydic acid and *o*-tolyl methyl ether; its 5'-*bromo*-derivative,  $\text{C}_{15}\text{H}_{11}\text{O}_3\text{Br}$ , m. p. 185—186°, gives an *acetyl* derivative,  $\text{C}_{17}\text{H}_{13}\text{O}_4\text{Br}$ , m. p. 131—132°; its 5'-*nitro*-derivative,  $\text{C}_{15}\text{H}_{11}\text{O}_5\text{N}$ , has m. p. 182°. 6'-*Hydroxyphenyl-m-tolyl-methane-2-carboxylic acid*,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , m. p. 215—216° (*silver salt*,  $\text{C}_{15}\text{H}_{13}\text{O}_3\text{Ag}$ ), obtained from the above phthalide by reduction with zinc dust and sodium hydroxide, is

converted by cold sulphuric acid into 2-hydroxy-3-methyl-9-anthrone,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix} \text{C}_6\text{H}_2\text{Me}\cdot\text{OH}$ , glistening prisms, m. p. 276—277°, which does not fluoresce in solution. It dissolves in cold potassium hydroxide solution, and by saturating the solution at 0° with carbon dioxide, a yellow precipitate, probably of the isomeric anthranol, is produced. By acetylation, the anthrone yields 2:9-diacetoxy-3-methylantracene,

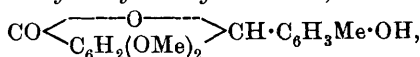


leaflets, m. p. 171—172°, which shows a blue fluorescence in acetic acid solution, and on oxidation with chromic acid gives 2-acetoxy-3-methylantraquinone,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_2\text{Me}\cdot\text{OAc}$ , needles, m. p. 177°, from which 3-hydroxy-2-methylantraquinone, m. p. 298·5° (Fraude, 1879), is obtained by hydrolysis. 3-*p*-Hydroxy-m-methoxyphenylphthalide,  $\text{CO} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CH}\cdot\text{C}_6\text{H}_3 \begin{smallmatrix} \text{OH} \\ | \\ \text{OMe} \end{smallmatrix}$ , m. p. 110·5—112·5°, from *o*-phthalaldehydic acid and guaiacol, gives an acetyl derivative,  $\text{C}_{17}\text{H}_{14}\text{O}_5$ , m. p. 142—143°, and, by reduction, 4'-hydroxy-3'-methoxydiphenylmethane-2-carboxylic acid,

$\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , m. p. 150—151° (silver salt,  $\text{C}_{15}\text{H}_{13}\text{O}_4\text{Ag}$ ). 2-Hydroxy-3-methoxy-9-anthrone,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix} \text{C}_6\text{H}_2 \begin{smallmatrix} \text{OH} \\ | \\ \text{OMe} \end{smallmatrix}$ , m. p. 211—213°, from the acid just mentioned, shows no fluorescence in solution, but dissolves in cold potassium hydroxide solution, and, on acetylation, gives 2:9-diacetoxy-3-methoxyanthracene,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C(OAc)} \\ | \\ \text{CH} \end{smallmatrix} \text{C}_6\text{H}_2 \begin{smallmatrix} \text{OAc} \\ | \\ \text{OMe} \end{smallmatrix}$ , m. p. 158·5—160·5°, from which 2-acetoxy-3-methoxyantraquinone,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_2 \begin{smallmatrix} \text{OAc} \\ | \\ \text{OMe} \end{smallmatrix}$ , m. p. 200·5—201·5°, is obtained by oxidation. This compound furnishes hystazarin monomethyl ether on hydrolysis. 3-*mp*-Dimethoxyphenylphthalide,

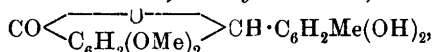


m. p. 144—145°, from *o*-phthalaldehydic acid and veratrole, suffers rupture of the lactonic ring when boiled in alcoholic solution with potassium hydroxide, and the resulting solution, on oxidation with potassium permanganate, gives *o*-3':4'-dimethoxybenzoylbenzoic acid (Lagodzinski, A., 1905, i, 82). By reduction of the phthalide, only a small quantity of the expected dimethoxydiphenylmethane-carboxylic acid is produced. The condensation of opianic acid with *o*-cresol to 6'-hydroxy-m-tolylmeconine,

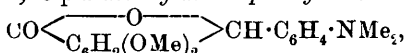


m. p. 181°, acetyl derivative, m. p. 137° (Winkler), is best carried out in presence of sulphuric acid; its methyl ether,  $\text{C}_{18}\text{H}_{18}\text{O}_5$ , m. p. 117·5—119°, may be obtained by methylation or from opianic

acid and *o*-tolyl methyl ether, and when boiled with dilute potassium hydroxide solution undergoes to a slight extent rupture of the lactonic ring. Neither the parent compound nor its methyl ether could be converted into a diphenylmethanecarboxylic acid by reduction. This was also the case with 3-*p*-hydroxy-*m*-methoxy-*meconine*,  $\text{CO} \langle \text{C}_6\text{H}_2(\text{OMe})_2 \rangle \text{CH} \cdot \text{C}_6\text{H}_3 \langle \text{OMe} \rangle_{\text{OH}}$ , m. p. 164–166°; 3-*mp*-dimethoxyphenylmeconine, m. p. 120·5–121·5°, yields tetramethoxy-*o*-benzoylbenzoic acid (Bentley and Weizmann, T., 1908, **93**, 437) on oxidation; 3-*orcyl*meconine,



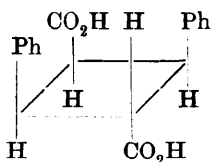
m. p. 223–225°; 3-*p*-dimethylaminophenylmeconine,



m. p. 132·5–134·5° (hydrochloride, needles), from opianic acid and dimethylaniline in presence of anhydrous oxalic acid, can also not be reduced by zinc dust and sodium hydroxide. Bistrzycki's 2-hydroxyanthranol (A., 1899, i, 151) is really 2-hydroxy-9-anthrone,  $\text{C}_6\text{H}_4 \langle \text{CO} \rangle_{\text{CH}_2} \text{C}_6\text{H}_3 \cdot \text{OH}$ , and, similarly, 2:3':4'-trimethoxydihydroanthrone is 3:4:7-trimethoxy-9-anthrone. 3-(*Nitro-β*-hydroxynaphthyl)-phthalide,  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{CH} \cdot \text{C}_{10}\text{H}_6 \langle \text{NO}_2 \rangle_{\text{OH}}$ , decomp. at 130·5°, is obtained by nitrating β-hydroxynaphthylphthalide.

J. K.

**Truxillic Acids. II.** R. STOERMER and E. EMMEL (*Ber.*, 1920, **53**, [B], 497–508. Compare Stoermer and Foerster, A., 1919, i, 444).—Further investigation of ε-truxillic acid leads the authors to the conclusion that it is an unusually stable *trans*-acid (annexed formula), the view being maintained that the truxillic acids and the isotruxillic acid are structural and not stereo-isomerides.



ε-Truxillic acid, long, colourless needles, m. p. 192° (identical with Hesse's β-cocaic acid), is conveniently prepared by protracted heating of α-truxillic acid with alkali hydroxide. It is not affected by prolonged heating or by drastic treatment with hydrochloric acid. Attempts to convert it into an internal anhydride were unsuccessful, but, by the action of acetic anhydride on the acid at 200–210°, or of phosphoryl chloride on the potassium salt, a non-crystalline anhydride of high molecular weight is obtained, which, however, is reconverted by water into ε-truxillic acid. The nature of the product is confirmed by its conversion by ethyl alcohol into *ethyl hydrogen ε-truxillate*, and by aniline into *ε-truxillidylanilide*, m. p. 284°, and *ε-truxillanilic acid*, needles, m. p. 293°.

The following derivatives of ε-truxillic acid are described: the *barium* and *calcium* salts, which are less soluble in hot than in cold water; methyl ester, m. p. 64°; *ethyl* ester, m. p. 34°; *chloride*,

m. p. 106—107°; *diamide*, small, transparent needles, m. p. 240°; *tetramethyldiamide*, m. p. 190°; *dianilide*, slender, silky needles, m. p. 284°.

The following investigations have been carried out in connexion with attempts to convert the truxillic acids into *cyclobutanetetra-carboxylic acids* (*loc. cit.*), but success has not been thus far achieved. Dinitro- $\gamma$ -truxillic acid, m. p. 293°, is most conveniently obtained by the action of fuming nitric acid (D 1.5) on the  $\gamma$ -anhydride, and is converted by acetic anhydride into dinitro- $\gamma$ -truxillic anhydride, small prisms, m. p. 229°. The acid is converted in the usual manner into *methyl dinitro- $\gamma$ -truxillate*, silky needles, m. p. 194°, *ethyl dinitro- $\gamma$ -truxillate*, glassy needles, m. p. 146°, and *dinitro- $\gamma$ -truxillyl chloride*, yellow prisms, m. p. 204°. The latter readily yields the corresponding *diamide*, pale yellow crystals, m. p. 280°, *tetramethyldiamide*, m. p. 276°, and *dianilide*, m. p. 261°. Dinitro- $\gamma$ -truxillic anhydride is transformed by aniline, according to conditions, either into *dinitro- $\gamma$ -truxillanilic acid*, m. p. 265°, or the corresponding *dianilide*; in contrast to the behaviour of  $\beta$ -isotruxillic anhydride, it could not be caused to yield an anil or a fluorescein derivative. With ethyl alcohol, it gives *ethyl hydrogen dinitro- $\gamma$ -truxillate*, long needles, m. p. 176—177°.

Ethyl dinitro- $\gamma$ -truxillate is reduced by hydrogen in the presence of palladium to *ethyl diamino- $\gamma$ -truxillate*, m. p. 162—163°; definite substances could not be isolated from the products of the oxidation of the hydrolysed ester by permanganate in acid or alkaline solution.

H. W.

**Bis-tropic Acids.** JULIUS VON BRAUN and LUDWIG NEUMANN (*Ber.*, 1920, **53**, [B], 594—601).—The experiments were undertaken with the pharmacologically interesting object of determining the extent to which it is possible to introduce doubly the group  $-\text{CH}(\text{CH}_2\cdot\text{OH})\cdot\text{CO}_2\text{H}$ , characteristic of tropic acid, into the aromatic nucleus. Unfortunately, the derivatives from *m*-xylene exhibit little tendency to crystallise, and cannot be distilled without decomposition, whilst the crystalline compounds from *o*- and *p*-xylenes could not be prepared on a sufficiently large scale owing to the prevalent scarcity of the parent hydrocarbons.

Ethyl *p*-phenylenediacetate readily condenses with ethyl formate in the presence of sodium and ether to yield *ethyl bishydroxy-methylene-p-phenylenediacetate*,  $\text{C}_6\text{H}_4[\text{C}(\text{:CH}\cdot\text{OH})\cdot\text{CO}_2\text{Et}]_2$ , m. p. 112—114°; the substance is immediately and completely soluble in dilute alkali or sodium carbonate solution, and in alcoholic solution gives an immediate, very dark bluish-violet coloration with ferric chloride. It readily yields a pale green, basic *copper salt*, and is transformed by aniline into the corresponding *dianilide*,  $\text{C}_6\text{H}_4[\text{C}(\text{:CH}\cdot\text{NHPh})\cdot\text{CO}_2\text{Et}]_2$ , crystalline powder, m. p. 143°. The *benzoyl* derivative has m. p. 186—187°. With phenylcarbimide, the ester yields diphenylcarbamide, owing to the unexpectedly ready elimination of water. Unlike ethyl and methyl formyl-

phenylacetates, the ester appears to have absolutely no tendency to pass into the ketonic form, and this fact appears to afford a certain amount of evidence against the aldo-enolic formulation of the former. An ethereal solution of the *p*-phenylene ester is readily reduced by activated aluminium (yield, 50%) to *ethyl p-phenylenebistropate* [*ethyl bishydroxymethyl-p-phenylenediacetate*],  $C_6H_4[CH(CH_2\cdot OH)\cdot CO_2Et]_2$ , m. p. 65—66°, which is hydrolysed by aqueous barium hydroxide to *p-phenylenebistropic acid*, shining leaflets, m. p. 93—94°.

*Ethyl m-phenylenediacetate*, colourless liquid, b. p. 196—198°/14 mm., condenses readily with ethyl formate, yielding a product which gives an intense bluish-violet coloration with ferric chloride, but which could only be obtained as a rather viscous, non-crystallisable oil, which decomposed when distilled even in a cathode vacuum. The reduction product is also an oil, whilst the acid corresponding with it could only be obtained as a sticky mass.

*Ethyl diformyl-o-phenylenediacetate*, prepared in the same manner as, but rather more readily than, the corresponding para-derivative, forms dark yellow crystals, m. p. 77—78°, and behaves solely as an enolic form. It is readily soluble in sodium carbonate, gives an intense bluish-green coloration with ferric chloride, a moss-green *copper* salt, and a dark yellow *anilide*, m. p. 200°. Like the para-compound, it loses water and forms diphenylcarbamide when treated with phenylcarbimide. Unlike the para-compound and all other formyl derivatives, however, it gives an intense permanganate-like coloration when its solution in alkali is shaken with benzoyl chloride, and an amorphous, violet precipitate rapidly separates. H. W.

### Formation and Stability of Associated Alicyclic Systems.

**I. A System of Nomenclature, and some Derivatives of Methane-II-cyclopropane and of Methane-III-cyclopropane.** RICHARD MOORE BEESLEY and JOCELYN FIELD THORPE (T., 1920, 117, 591—620).

**Preparation of Mellitic Acid.** RICHARD LORENZ and JULIUS HAUSMANN (D.R.-P. 318200; from *Chem. Zentr.*, 1920, ii, 492).—Mixtures of finely divided carbon or soot with tar, pressed into rods or plates and subsequently heated in the absence of air, are subjected to anodic oxidation in an alkaline electrolyte; the liberated hydrogen may be obtained as by-product if a diaphragm is used. Soot may be replaced by other finely divided varieties of carbon, such as wood charcoal, lamp-black, or gas carbon, either alone or in admixture with soot. Solutions of sodium or potassium hydroxide, or of alkali carbonates or hydrogen carbonates, may be used as electrolytes. H. W.

**Some Derivatives of 2 : 4-Dinitrobenzaldehyde.** ALEXANDER LOWY and BLAINE B. WESCOTT (*J. Amer. Chem. Soc.*, 1920, 42, 849—856).—A number of condensation products of 2 : 4-di-

nitrobenzaldehyde with aromatic amines are described. No evidence of stereoisomerism could be observed among them, and attempts to isolate the intermediate additive compounds were unsuccessful.

2:4-Dinitrobenzylidene-*m*-toluidine,  $C_6H_3(NO_2)_2 \cdot CH:N \cdot C_6H_4Me$ , yellow needles, m. p.  $130^\circ$ ; 2:4-dinitrobenzylidene-*m*-4-xylylidene,  $C_6H_3(NO_2)_2 \cdot CH:N \cdot C_6H_3Me_2$ , yellow needles, m. p.  $210.5^\circ$ ; 2:4-dinitrobenzylidene-3-nitro-*p*-toluidine,

$C_6H_3(NO_2)_2 \cdot CH:N \cdot C_6H_3Me \cdot NO_2$ , yellow needles, m. p.  $195^\circ$ ; 2:4-dinitrobenzylidene- $\psi$ -cumidine,  $C_6H_3(NO_2)_2 \cdot CH:N \cdot C_6H_2Me_3$ , yellow needles, m. p.  $186.5^\circ$ ; sodium 2:4-dinitrobenzylidenesulphanilate,

$C_6H_3(NO_2)_2 \cdot CH:N \cdot C_6H_4 \cdot SO_3Na \cdot H_2O$ , pale yellow crystals, decomposing at  $249^\circ$ ; sodium 2:4-dinitrobenzylidenemetanilate ( $3H_2O$ ), yellow needles, decomposing at  $185^\circ$ ; sodium 2:4-dinitrobenzylidenenaphthionate,

$C_6H_3(NO_2)_2 \cdot CH:N \cdot C_{10}H_6 \cdot SO_3Na \cdot \frac{1}{2}H_2O$ , orange needles, decomposing at  $248^\circ$ . By condensation with dimethylaniline, 2:4-dinitrobenzaldehyde yields a green dye, doubtless a derivative of malachite-green. J. K.

**Constitution of the Methylcyclohexanone prepared by Ethylation of 1-Methylcyclohexan-6-one.** A. HALLER and R. CORNUBERT (*Compt. rend.*, 1920, **170**, 973—976).—The compound previously prepared by the ethylation of 1-methylcyclohexan-6-one in the presence of sodamide (compare A., 1913, i, 984) is shown to be 1-ethyl-1-methylcyclohexan-6-one. Like dimethylcyclohexanone (compare this vol., i, 390), it gives a benzylidene derivative, which is 5-benzylidene-1-methyl-1-ethylcyclohexan-6-one, m. p.  $78-78.5^\circ$ , and a compound,  $C_{23}H_{26}O_2$ , m. p.  $148-150^\circ$ .

W. G.

#### Hydroxycarbonyl Compounds. IV. Synthesis of Aspidinol.

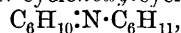
P. KARRER and FR. WIDMER (*Helv. Chim. Acta*, 1920, **3**, 392—395. Compare A., 1919, i, 160, 592, 594).—By condensation of butyronitrile with methyl phloroglucinol  $\beta$ -mono-methyl ether in presence of hydrogen chloride, a mixture of two ketones,  $OMe \cdot C_6HMe(OH)_2 \cdot COPr^a$ , was produced, which can be resolved into its components by fractional crystallisation from light petroleum. The less soluble, m. p.  $140-141^\circ$ , gave a green colour with ferric chloride, and its identity with aspidinol (Böhm, A., 1902, i, 37) was established by direct comparison. The more soluble, needles, m. p.  $116.5^\circ$ , gave a deep brownish-red colour with ferric chloride, and was called  $\psi$ -aspidinol. The two compounds are doubtless the 3- and the 5-butyryl derivatives of the original compound, of which aspidinol has been considered to be the 3-butyryl derivative (Böhm); but this would be contrary to the rule that in such compounds the isomeride with the ketonic group in the para-position to the methoxyl group has a lower melting



point and a greater solubility in light petroleum than the ortho-isomeride (Karrer, A., 1919, i, 592). The distribution of the formulæ between the two compounds is therefore left undecided.

J. K.

**The Ketimines: Formation by Catalytic Reduction of Oximes.** GEORGES MIGNONAC (*Compt. rend.*, 1920, 170, 936—938).—Ketoximes may be reduced in solution in absolute alcohol in the presence of reduced nickel by shaking the solution with hydrogen under atmospheric pressure. The action should be stopped when one molecule of hydrogen has been absorbed for one molecule of oxime. The resulting ketimines undergo hydrolysis by traces of moisture with varying degrees of readiness. In this way, cyclohexanoneoxime yielded N-cyclohexylcyclohexylideneketimine,

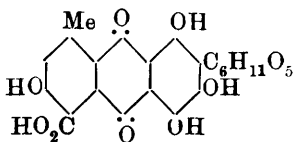


b. p. 117—118°/9 mm.,  $D_4^{21}$  0.940,  $n_D^{21}$  1.4972, giving a hydrochloride, m. p. 180° (decomp.). Acetophenoneoxime yielded phenylmethylketimine,  $\text{CPhMe}\cdot\text{NH}$ , isolated as its hydrochloride. Propiophenoneoxime gave phenylethylketimine, yielding a hydrochloride, m. p. 145°, an acetyl derivative, m. p. 126°, and a condensation product, N- $\alpha$ -phenylpropylphenylethylketimine,  $\text{CPhEt}\cdot\text{N}\cdot\text{CHEtPh}$ , b. p. 170—171°/9 mm. Benzophenoneoxime yielded diphenylketimine,  $\text{CPh}_2\cdot\text{NH}$ , and phenyl- $\alpha$ -naphthylketoxime gave phenyl- $\alpha$ -naphthylketimine,  $\text{C}_{10}\text{H}_7\cdot\text{CPh}\cdot\text{NH}$ , m. p. 68—69°. The imine group appears to become more stable with respect to water as the groups attached to it become more electronegative in character, the stability of the ketimines described above increasing in the order in which they are given.

W. G.

**Carminic Acid.** OTTO DIMROTH and HANS KÄMMERER (*Ber.*, 1920, 53, [B], 471—480).—It has been shown previously (A., 1913, i, 977) that carminic acid is a hydroxyanthraquinone, and the similarity of its absorption spectra and tinctorial properties to those of kermes dye (A., 1916, i, 561) points to the conclusion that it, like the latter, is a hydroxyanthrapurpurin. This is now shown to be the case. It is also found that complete acetylation of carminic acid yields an octa-acetyl derivative. Since, however, only four hydroxyl groups are present in the anthraquinone nucleus, it follows that the remaining four must be present in the side-chain, to which the composition  $\text{C}_6\text{H}_{13}\text{O}_5$  has been previously assigned. If, now, one oxygen atom of the latter is present in an ethereal, aldehydic, or ketonic form, a modification of the formula becomes essential, and the side-chain is now considered to be  $\text{C}_6\text{H}_{11}\text{O}_5$ , the alteration being found to give calculated values which agree with the observed analytical data as well as did those based on the older formula. The constitution of the side-chain has not been fully elucidated. It appears probable that it has a sugar-like structure, although carminic acid is certainly not a glucoside. It contains at least one asymmetric carbon atom, since carminic acid is now found to be optically active, and this phenomenon cannot be attributed to the structure of the nucleus, since kermesic

acid, and also the less closely related laccaic acid, are optically inactive. The structure of carminic acid, as far as it has been elucidated, is expressed by the annexed formula.



Under suitable conditions, carminic acid is reduced by zinc dust and glacial acetic acid to a leuco-compound, which is converted by atmospheric oxidation into *deoxycarminic acid*, yellowish-red needles, which is best purified by conversion into its *acetyl* derivative, orange-yellow needles, m. p. 245—250° (decomp.). The loss of a  $\beta$ -hydroxyl group during the reduction has its parallel in the cases of kermesic acid and hydroxyanthrapurpurin (Dimroth and Fick, A., 1916, i, 561), whilst the presence of two hydroxyl groups in the 1:4-position relative to one another in the reduction product is shown by its oxidation to a diquinone, from which carminic acid is regenerated by the action of acetic anhydride and sulphuric acid.

Octa-acetylcarmine acid is most conveniently prepared by the action of acetic anhydride and a little concentrated sulphuric acid on carminic acid at the ordinary temperature. When, however, carminic acid is warmed with acetic anhydride in the absence of a catalyst, a *hexa-acetyl* derivative, yellowish-red, cubic crystals, which soften and decompose at 170°, is smoothly formed; two hydroxyl groups in the  $\alpha$ -positions on the nucleus remain unaffected, since the substance is readily converted by lead tetra-acetate into an unstable diquinone, which is reduced by sulphurous acid to the parent substance.

Carminic acid has  $[\alpha]_{D}^{25} + 51.6^\circ$  in aqueous solution, whilst octa-acetylcarmine acid has  $[\alpha]_{D}^{25} + 80.55^\circ$  in chloroform. Deoxycarminic acid is strongly active, but the acetyl derivatives of kermesic and laccaic acids are completely inactive. H. W.

**The Acetylation of Hydroxyanthraquinones and Anthra-diquinones.** OTTO DIMROTH, OTTO FRIEDEMANN, and HANS KÄMMERER (*Ber.*, 1920, **53**, [B], 481—487).—In connexion with the observations made during the acetylation of carminic acid (preceding abstract), the authors have investigated the behaviour of various hydroxyanthraquinones when similarly treated, and find that, quite generally, the hydroxyl groups in the  $\alpha$ -position are far less readily attacked than those in the  $\beta$ -position. A convenient method for the preparation of  $\beta$ -acetylated derivatives consists in allowing calculated quantities of acetic anhydride and the hydroxy-compound to react in cold pyridine solution; with an excess of anhydride, the  $\alpha$ -hydroxy-groups are also attacked.

2-Hydroxyanthraquinone is completely acetylated when boiled for ten minutes with acetic anhydride, whilst, under similar conditions, 1-hydroxyanthraquinone is scarcely attacked; after six hours' treatment, however, the latter is largely acetylated. *Purpurin 2-acetate*, prepared from the components in hot pyridine solution, forms orange-coloured crystals, m. p. 172—173°, and is oxidised by lead peroxide or lead tetra-acetate to *2-acetylpurpurin-*

quinone, straw-yellow, slender needles, m. p. 167—168°. *Alizarin-bordeaux* 2-acetate,  $C_6H_2(OH)_2$   $\begin{matrix} \text{CO} \cdot \text{C} \cdot \text{C}(\text{OH}) : \text{C} \cdot \text{OAc} \\ | \\ \text{CO} \cdot \text{C} \cdot \text{C}(\text{OH}) : \text{CH} \end{matrix}$ , forms red needles, m. p. 246—247°. *Hydroxyanthrapurpurin* 2:7-diacetate crystallises in orange-coloured needles, m. p. 224—225°, and is oxidised by lead tetra-acetate to an unstable diquinone, which was not obtained in the crystalline condition.

An improved process for the oxidation of quinizarin to 1:4:9:10-anthradiquinone, either by means of lead peroxide or lead tetra-acetate, has been worked out (compare Dimroth and Schultze, A., 1916, i, 563). In a similar manner, mono- and dibromoquinizarin are oxidised to 3-bromo-1:4:9:10-anthradiquinone, straw-yellow, flat needles, m. p. 212—214° (decomp.), and 2:3-dibromo-1:4:9:10-anthradiquinone, yellowish-green, six-sided leaflets, which become red without melting at 300°, respectively.

Purpurinquinone 2-acetate is transformed by acetic anhydride and sulphuric acid into tetra-acetoxyanthraquinone, m. p. 205°, which is hydrolysed to 1:2:3:4-tetrahydroxyanthraquinone.

H. W.

**Constituents of Indian Turpentine from *Pinus longifolia*, Roxb.** I. JOHN LIONEL SIMONSEN (T., 1920, 117, 570—578).

**Hot Vulcanisation of Caoutchouc.** F. KIRCHHOF (*Kolloid Zeitsch.*, 1920, 26, 168—173).—A theoretical paper in which the author criticises the views of Harries (*Untersuch. natürlich. Künstlich. Kautschukarten*) (A., 1916, i, 659). The author claims that, previously to Harries, he had put forward the physico-chemical principles on which the hot vulcanisation of rubber takes place. Several experiments with lead oxide and lead sulphide mixed with small quantities of sulphur and a small quantity of sulphur-free organic catalyst are described, which show that vulcanisation can be effected with other substances than sulphur. In view of the advances in the knowledge of the constitution of rubber by the work of Harries, and the behaviour of depolymerised rubber on bromination (Schmitz, *Gummi Zeit.*, 1919, 34, 1937), it is held that the chemical interpretation of the vulcanisation process is likely to undergo many modifications.

J. F. S.

**Artemisin.** P. BERTOLO (*Gazzetta*, 1920, 50, i, 109—113).—The conclusions concerning the constitution of artemisin drawn from the author's previous investigations (A., 1904, i, 177; 1905, i, 224, 897; 1908, i, 560; 1911, i, 898) are briefly summarised. Short descriptions are now given of the products obtained by the action of various reagents on artemisin; the constitutions of these products are to be discussed later.

The action of dilute sulphuric acid (1:1) on artemisin at temperatures below 60° yields a white, crystalline compound, m. p. 236°,  $[\alpha]_D - 84.16^\circ$ , insoluble in alkali carbonate solution, but soluble in alkali hydroxide solution, from which it is precipitated unaltered by means of carbon dioxide; in this compound, the

lactonic linking is preserved, but not the ketonic carbonyl, which appears to be converted into the phenolic group,  $C\cdot OH$ , with formation of a desmotropo-artemisin. The action of more concentrated sulphuric acid at  $100^{\circ}$  gives a red oil, which solidifies on cooling and dissolves almost completely in alkali carbonate solutions, and appears to be identical with the dextrorotatory artemisic acid obtained by the action of hydrochloric acid on artemisin.

Treatment of artemisin with hydriodic acid and red phosphorus yields an acid compound, which somewhat resembles artemisic acid, but has the lower m. p.  $98^{\circ}$  and the higher specific rotation  $[\alpha]_D +72.3^{\circ}$ . This compound forms white crystals, but gradually reddens and partly resinifies on exposure to light. It is also formed when artemisin is treated with iodine in alcoholic solution, and is probably a product of the further reduction of artemisic acid, from which it is apparently formed by reduction with sodium amalgam.

Acetic anhydride does not act on artemisin, but acetyl chloride converts it into the pale yellow *acetyl* compound,  $C_{15}H_{17}O_4Ac$ , m. p.  $200^{\circ}$ ,  $[\alpha]_D -52.60^{\circ}$ , which, when hydrolysed with potassium hydroxide, gives, not artemisin, but a moderately stable acid compound, m. p.  $200^{\circ}$ .

According to the conditions employed, the action of chlorine on artemisin yields one of three chloro-derivatives, m. p.  $135^{\circ}$ ,  $230^{\circ}$ , and  $180^{\circ}$  respectively.

Reduction of artemisin by means of sodium amalgam gives, in almost theoretical yield, a crystalline, optically inactive, acid compound, m. p.  $170^{\circ}$ , the *barium* salt and *ethyl* ester of which have been analysed.

Exposure to light of a solution of artemisin in 50% acetic acid for about two months at a temperature never exceeding  $35^{\circ}$  results in the formation mainly of a white, crystalline compound, m. p.  $242^{\circ}$ , which exhibits lactonic and phenolic functions, and appears to be a new desmotropic form of artemisin. Exposure of the same solution to light during the summer months, when the temperature may sometimes reach  $45^{\circ}$ , yields principally a white acid, m. p.  $168^{\circ}$ .

Barium hydroxide on heating strongly attacks artemisin, giving ill-defined decomposition products; from the resinous substances obtained, an acid compound, m. p.  $168^{\circ}$ , which does not react with phenylhydrazine, was with difficulty isolated in an impure condition.

T. H. P.

**Action of Sulphuric Acid on Artemisin:** *desmotropo-Artemisin*. P. BERTOLO (*Gazzetta*, 1920, 50, i, 114—119. Compare preceding abstract).—l-desmotropo-Artemisin,  $C_{15}H_{18}O_4$ , prepared by the action of dilute sulphuric acid on artemisin at temperatures below  $60^{\circ}$ ; forms white, flattened crystals, m. p.  $236^{\circ}$ , and, when treated with boiling solutions of alkali or alkaline-earth hydroxides, yields the corresponding salts of an unstable, monobasic hydroxy-acid; when the latter is liberated, it undergoes ready conversion into the original lactone. With sulphuric

acid and ferric chloride, *l*-desmotropo-artemisin gives neither the santonin nor the artemisin reaction, but remains undissolved and without coloration even in the hot.

In aqueous solution, the *barium* salt,  $(C_{14}H_{19}O_3 \cdot CO_2)_2Ba$ , gives: with silver nitrate, the flocculent *silver* salt, which turns brown in the light and decomposes with formation of a silver mirror in the hot; with copper sulphate, a bluish-white precipitate; with lead acetate, a flocculent, white precipitate, somewhat soluble in excess of the reagent; with ferric chloride in the cold, no precipitate, whereas in the hot, a red, flocculent precipitate slowly forms.

*Acetyl-l*-desmotropo-artemisin,  $C_{15}H_{17}O_3 \cdot OAc$ , forms aggregates of radiating, shining crystals, m. p. 154—155°,  $[\alpha]_D - 66 \cdot 90^\circ$ .

Zinc dust and acetic acid are without action on *l*-desmotropo-artemisin, no acid analogous to the santonous acids being obtained in this way.

T. H. P.

### Rutin, the Flavone Pigment of *Escholtzia californica*, Cham.

CHARLES E. SANDO and H. H. BARTLETT (*J. Biol. Chem.*, 1920, **41**, 495—501).—Nearly 5% of rutin is present in the petals of *Escholtzia californica*. It crystallises in fine, dense tufts of silky crystals, m. p. 190—192° (uncorr.). The accepted constitution of rutin (quercetin-glucoso-rhamnoside) is supported. Quercetin, m. p. 310°, glucosazone, and rhamnosazone were isolated after acid hydrolysis.

J. C. D.

### Solubilities of Theobromine.

RAYMOND V. WADSWORTH (*Analyst*, 1920, **45**, 133—134).—The recorded solubilities for theobromine are inaccurate, the error apparently originating with Mitscherlich, whose values for the solubility of the alkaloid in chloroform, ether, and water are much too high. The impurity to which this is to be attributed appears to have been caffeine. The following amounts of pure theobromine were dissolved by different solvents at 15·5° and at their boiling points respectively: ethyl ether, 0·003 and 0·003; benzene, 0·005 and 0·010; carbon tetrachloride, 0·020 and 0·040; chloroform, 0·060 and 0·070; boiling absolute alcohol, 0·100; water, 0·060 and 0·700; tetrachloroethane, 0·090 and 0·870; and aniline, 0·650 and 8·000%.

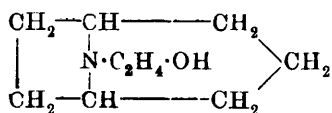
C. A. M.

### The Tropine and Cocaine Series. II.

JULIUS VON BRAUN and KURT RÄTH (*Ber.*, 1920, **53**, [B], 601—614).—In continuation of previous work (von Braun and Müller, A., 1918, i, 233), the authors have further examined the influence of the relative positions of the hydroxyl group and the basic nitrogen atom and of the introduction of double bonds on the physiological activity of the tropeines. Sufficient evidence has not, however, been collected to enable any general conclusion to be drawn with regard to mydriatic action. The anæsthetic power, however, seems to attain its maximum when the hydroxyl group is in the  $\gamma$ -position to the nitrogen atom, and, if this condition is fulfilled, to be independent of any

special mode of attachment of the hydroxyl group within the molecule. It is also increased by the introduction of double bonds into the seven-membered carbon ring.

Tropane is most conveniently converted into nortropane according to the method of Willstätter and Iglauder, an elaboration of



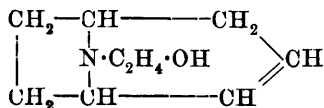
which is fully described. The latter is transformed by ethylene oxide into N- $\beta$ -hydroxyethylnortropine (annexed formula), viscous oil, b. p. 127—128°/13 mm., which yields a *hydrochloride*, colourless, hygroscopic needles, m. p.

157°, a *platinichloride*, red needles, which decompose at 194—196°, a *picrate*, long, yellow needles, m. p. 181°, a *methiodide*, leaflets, m. p. 261°, and an oily *benzoyl* derivative (*hydrochloride*, m. p. 118°). Introduction of the tropic acid residue is effected in the manner previously adopted with mydriasin (*loc. cit.*); the substituted *amine*, however, is an oil, and yields a non-crystalline *hydrochloride*, *hydrobromide*, *oxalate*, *aurichloride*, and *platinichloride*. The *methiodide* forms colourless leaflets, m. p. 137—138°.

N- $\gamma$ -Hydroxypropylnortropane is prepared in the form of its oily *benzoyl* derivative (*hydrochloride*, crystalline powder, m. p. 162°) by the action of  $\gamma$ -bromopropyl benzoate on nortropane; it is a colourless, moderately viscous liquid, b. p. 141—143°/22 mm., and forms a *picrate*, yellow needles, m. p. 121°, a *hydrochloride*, m. p. 155°, *platinichloride*, slender, yellow needles, m. p. 166°, and *methiodide*, m. p. 261°. N-*p*-Nitrobenzoyl- $\gamma$ -oxypropylnortropane, m. p. 40° (*hydrochloride*, m. p. 236°; *picrate*, m. p. 186°), is prepared from the tropane and *p*-nitrobenzoyl chloride, and is reduced by stannous chloride to the *p*-aminobenzoyl base, which is an odourless, viscous oil (*dihydrochloride*, m. p. 215—216° after softening at 211°; *platinichloride*, m. p. 217° [decomp.]; *picrate*, m. p. 150°); the *acetyl* derivative could only be obtained as an oil, which gives a *picrate*, yellow, crystalline powder, m. p. 113°. The introduction of the new amino-group has very little effect on the physiological action of the base, probably since it does not markedly increase the already basic properties.  $\gamma$ -Hydroxypropylnortropane is converted into its *tropate* in the same manner as the corresponding  $\beta$ -derivative. Like the homologous tropeine, however, it is an oil, and yields oily salts; the *methiodide* is crystalline and has m. p. 111°.

N- $\epsilon$ -Hydroxyamylnortropane is obtained as an oily *benzoyl* derivative (*hydrochloride*, m. p. 181°; *platinichloride*, m. p. 176°; *picrate*, m. p. 112—113°) by the action of  $\epsilon$ -bromoamyl benzoate on nortropane; it is a transparent, rather viscous liquid, b. p. 174—176°/20 mm., which yields a *picrate*, yellow leaflets, m. p. 97°, a *platinichloride*, yellow needles, m. p. 202°, and a crystalline *methiodide*, which does not melt below 270°. The corresponding *tropheine* is obtained by the aid of acetylpropyl chloride; it is an oil, which only yields oily derivatives.

*N*-β-Hydroxyethylnortropidine (annexed formula), colourless, rather viscous oil, b. p. 115—117°/12 mm., is prepared by the action of ethylene oxide on nortropidine in chloroform solution in the presence of a trace of water; it gives a *platinichloride*, long, yellow needles, m. p.



158°, a *picrate*, orange leaflets, m. p. 162°, and a coarsely crystalline *methiodide*, which does not melt below 270°. The *benzoyl* derivative is an oil, the *hydrochloride* of which has m. p. 184°. The *tropyl* derivative closely resembles that obtained from ε-hydroxyamylnortropine; the oily *methiodide* could, however, be converted into a crystalline *platinichloride*,  $\text{C}_{38}\text{H}_{52}\text{O}_6\text{N}_2\text{Cl}_6\text{Pt}$ , yellow, crystalline powder, m. p. 139° (decomp.), after darkening above 120°.

The *benzoyl* derivative of *N*-γ-hydroxypropylnortropidine, prepared from nortropidine and γ-bromopropyl benzoate, is a moderately viscous, non-crystallisable oil, which yields a *hydrochloride*, m. p. 165—167°. It appears to be smoothly hydrolysed to *N*-γ-hydroxypropylnortropidine, but lack of material prevented the fuller investigation.

H. W.

### Triphenylpyridine, Acetophenone, and Acetophenine.

W. DILTHEY and F. KIEFER (*Ber.*, 1920, **53**, [B], 621—622).—It has been shown recently by Reddelien (this vol., i, 316) that Engler's acetophenone [described in the latest edition of Beilstein's *Handbuch* as acetophenine] is identical with triphenylpyridine. This is confirmed by the authors, who have further prepared the trinitrotriphenylpyridine described by Engler and Heine. Like Reddelien, they find that the yields of triphenylpyridine obtainable from acetophenone and benzaldehyde or benzonitrile are very small, and consider the substance to be most conveniently prepared by the action of ammonia on arylated pyrilium salts.

H. W.

**Formation of 4-Benzyl-3-methyl-5-pyrazolone.** FRANCESCO CHERCHI (*Gazzetta*, 1920, **50**, i, 120—127).—4-Benzyl-3-methyl-5-pyrazolone,  $\text{CO} \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{CH}(\text{CH}_2\text{Ph}) \cdot \text{CMe} \end{array}$ , obtained by the action

of hydrazine hydrate on methyl or ethyl α-benzylacetoacetate in aqueous-alcoholic solution, forms white needles, m. p. 228—229°. When treated in alcoholic solution with sodium ethoxide, it yields the *sodium salt*,  $\text{C}_{11}\text{H}_{11}\text{ON}_2\text{Na}$ , and a *compound*, which crystallises in needles, m. p. 141—142°. The *picrate*,  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_6\text{H}_3\text{O}_7\text{N}_3$ , forms yellow needles, m. p. 154.5°. 1(?) *-Acetyl-4-benzyl-3-methyl-5-pyrazolone*,  $\text{C}_{11}\text{H}_{11}\text{ON}_2\text{Ac}$ , forms silky, white needles, m. p. 128—129°.

4-Benzyl-3-methyl-1(?) *-ethyl-5-pyrazolone*,  $\text{C}_{11}\text{H}_{11}\text{ON}_2\text{Et}$ , prepared by the action of ethyl iodide on the pyrazolone dissolved in sodium ethoxide solution, crystallises in large, colourless prisms,

m. p. 177°, and is accompanied by a yellow, oily compound, which is to be investigated later.

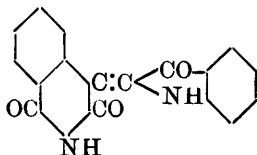
T. H. P.

**Dibutylbarbituric Acid.** O. KAMM and E. H. VOLLWEILER (U.S. Pat. 1331712).—To the solution of 40 grams of sodium in 1000 c.c. of absolute alcohol are added 157 grams of ethyl dibutylmalonate (prepared by the interaction of butyl bromide and ethyl malonate in the presence of 2 mols. of sodium ethoxide) and 50 grams of carbamide, and the mixture is heated for six hours under pressure at 100—110°. The alcohol is then removed by distillation, water is added, and dibutylbarbituric acid, colourless needles, m. p. 158°, is precipitated by hydrochloric acid, the yield being 130 grams. The substance has pronounced sedative properties with but slight toxicity.

CHEMICAL ABSTRACTS.

**The Cyanine Dyes. I. The Constitution of the *iso*Cyanines.** WILLIAM HOBSON MILLS and ROBERT SCOTT WISHART (T., 1920, 117, 579—587).

**Dyes Derived from 1:3-Dioxyisoquinoline** [*o*-Homophthalimide]. W. HERZOG (*Ber.*, 1920, 53, [B], 564—567).—Homophthalimide is readily condensed with  $\alpha$ -isatinanilide in acetic anhydride solution to yield 1:3-dioxy-4-isoquinoline-2'-indoleindigo [1:3-diketo-4-(2')-indoxyltetrahydroisoquinoline] (annexed formula), reddish-violet, amorphous powder, m. p. about 270°, which is readily decomposed by dilute solutions of alkali hydroxides, but can be converted into its leuco-compound by zinc dust and acetic acid; it gives dark violet shades on wool.



Similarly,  $\beta$ -isatinanilide yields 1:3-dioxy-4-isoquinoline-3'-indoleindigo [1:3-diketo-4-(3')-indoxyltetrahydroisoquinoline], brown needles, m. p. about 300°, which is slowly decomposed by cold alkali hydroxide solutions. It can be reduced by hyposulphite in the presence of alkali or by zinc and acetic acid, but the vat is devoid of tinctorial properties. 1:3-Dioxy-4-isoquinoline-2'-thionaphthenindigo [1:3:3'-Tri keto-4-(2')-thionaphthentetrahydroisoquinoline], from *o*-homophthalimide and thionaphthenquinoneanilide, crystallises in yellowish-red needles, m. p. about 250° (decomp.). The leuco-compound can be prepared in the usual manner, but has little affinity for the fibres, giving fugitive cherry-red shades on wool and pale pink tones on cotton.

H. W.

**The Stabilisation of Nitrous Acid in Connexion with Reactions carried out with this Compound; Applications to Diazotisation.** E. BRINER and R. JONAS (*Helv. Chim. Acta*, 1920, 3, 366—369).—The reversibility of the decomposition of nitrous acid into nitric acid, nitric oxide, and water suggests that solutions of the acid should be stable in presence of nitric oxide under pressure. This principle has been successfully applied to



the diazotisation of dinitroaniline, tribromoaniline, and *p*-sulphobenzeneazo- $\alpha$ -naphthylamine, which is difficult under ordinary conditions, by condensing nitrogen trioxide in a cooled tube containing the amino-compound and hydrochloric acid, sealing the tube, and allowing the temperature to rise. Picramide was not diazotised by this treatment. The value of the use of compressed air, proposed in the case of the last of the above three compounds (D.R.-P. 143450), is probably to be explained in the same way.

J. K.

**Origin of the Humin formed by the Acid Hydrolysis of Proteins. V.** ROSS AIKEN GORTNER and GEORGE E. HOLM (*J. Amer. Chem. Soc.*, 1920, **42**, 821—827. Compare this vol., i, 400).—Pursuing their inquiry as to the nature of the reaction by which humin is produced, the authors prepared artificial mixtures of thirteen of the amino-acids commonly obtained by the hydrolysis of proteins. Such mixtures, when boiled for twenty-four hours with hydrochloric acid in presence of either trioxymethylene or tyrosine and trioxymethylene, or tryptophan and tyrosine, gave no insoluble humin; but this was produced when tryptophan, tyrosine, and formaldehyde were present. The reaction is therefore dependent on the presence of tryptophan, and can serve as a quantitative measure of the amount of this substance present. Similarly, soluble humin is derived from tyrosine, but, owing to its solubility, the amount is not a quantitative measure of the tyrosine. Phosphotungstic humin was produced to an equal extent in all the experiments, and may represent only an adsorption phenomenon. It is specially noted that the amino-group of cystine was not displaced in these experiments.

J. K.

**The Action of Thrombin on Fibrinogen.** JOHN OGLETHORPE WAKELIN BARRATT (*Biochem. J.*, 1920, **14**, 189—209).—Fibrinogen in solution is diphasic, consisting of a concentrated phase which is dispersed, and a dilute phase which is continuous.

The action of thrombin is to form fibrin only from the fibrinogen in the concentrated phase, and is purely catalytic. A hypothesis of the mode of formation of fibrin fibrils is advanced. When fibrinogen in the concentrated phase is converted into fibrin, the equilibrium between the phases is disturbed, and more fibrinogen passes from the continuous to the disperse phase. This is then converted into fibrin. The "growth" of fibrin fibrils proceeds at a unimolecular rate.

J. C. D.

**The Mode of Union of Iron in the Prosthetic Group of Blood Pigments and the Constitution of Hæmin.** WILLIAM KÜSTER (*Ber.*, 1920, **53**, [B], 623—633).—The communication is mainly devoted to a reasoned, adverse criticism of the views propounded by Willstätter (*A.*, 1915, i, 289). The author maintains his ideas (*A.*, 1912, i, 670) that two of the nitrogen atoms in hæmin are basic, and are so related to the two carboxyl groups that one nitrogen is united to one carboxyl group as

a betaine complex, leaving one carboxyl group, which alone can be easily esterified. In support of this hypothesis, it is now shown that the *diethyl ether* of *haematoporphyrin*, red, crystalline powder without a distinct melting point (the *silver* salt and the very hygroscopic *dihydrochloride* are described), is transformed by a boiling 1% solution of hydrogen chloride in ethyl alcohol into an isomeric *diethyl ether*, needles (and is thus not esterified), which is slowly converted by *N*-hydrochloric acid into the dihydrochloride of the original material; with more concentrated alcoholic hydrochloric acid solution, *haematoporphyrin diethyl ether* is converted into *tetraethylhaematoporphyrin*, steel-blue powder, m. p. about 91—93°. The action of diazomethane on *hæmin* has been investigated previously (A., 1918, i, 199), and this is now shown to differ fundamentally from its effect on the hydrochlorides of the triphenylmethane dyes, since, in the former class, the halogen atom is never removed, whilst in the latter series it is eliminated as methyl chloride, and the leucobase is formed. It is therefore probable that the halogen atom is directly united to the iron atom, and this is rendered more probable, since measurement of the electrolytic conductivity of *hæmin* and its dimethyl ester in pyridine solution shows them to behave in the same manner as inorganic salts.

H. W.

**Refractivity of Hæmoglobin in Solution.** FREDERICK H. HOWARD (*J. Biol. Chem.*, 1920, **41**, 537—547).—The refractive index of hæmoglobin solutions varies directly with concentration and is independent of the presence of other proteins, and of bases and salts in low concentration. The value of *a* for hæmoglobin is 0.00183.

J. C. D.

**Hæmocyanin.** III. CH. DHÉRÉ (*J. Physiol. Path. gén.*, 1919, **18**, 503—526; from *Physiol. Abstr.*, 1920, **5**, 7).—Hæmocyanin of the snail can be obtained in a crystalline form by dialysis against distilled water, by exposing the blood to a potential difference of 120 volts after dialysis, or cooling the supernatant liquid in the dialyser in ice. It may be purified by solution in a very small amount of *N*/500-sodium sulphate, from which it crystallises on cooling in ice. Hæmocyanin of the rock lobster can be crystallised by the last method, and that of cephalopods by the method of Hopkins and Pinkus, using concentrated ammonium sulphate. The varying forms of crystals obtained are probably due to differences in the proportions of water of imbibition, not of hydration.

W. G.

**Properties of the Nucleotides obtained from Yeast Nucleic Acid.** P. A. LEVENE (*J. Biol. Chem.*, 1920, **41**, 483—493).—The work reported in this paper was carried out in order to clear up the discrepancies in the reported properties of the nucleotides from yeast.

Adenosinephosphoric acid,  $C_{10}H_{14}O_7N_6P, H_2O$ , is the most insoluble of the four nucleotides. It decomposes with effervescence at 195°

(corr.);  $[\alpha]_D^{20} - 40.5^\circ$  in 1% aqueous solution,  $-40.5^\circ$  to  $-44.5^\circ$  in 5% aqueous-ammonia solution;  $[\alpha]_D^{20} - 38.0^\circ$  in 10% hydrochloric acid,  $-59.5^\circ$  in 2% sodium hydroxide,  $-66.0^\circ$  in 5% sodium hydroxide.

Guanosinephosphoric acid,  $C_{10}H_{14}O_8N_5P \cdot 2H_2O$ , contracts on heating at  $175^\circ$  (corr.) and decomposes at  $180^\circ$ .  $[\alpha]_D^{25} - 7.5^\circ$  in water,  $+1.5^\circ$  in 10% hydrochloric acid;  $[\alpha]_D^{20} - 44.0^\circ$  in 5% aqueous ammonia;  $[\alpha]_D^{25} - 57.0^\circ$  in 2% aqueous sodium hydroxide,  $-65.0^\circ$  in 5% aqueous sodium hydroxide.

Cytidinephosphoric acid,  $C_9H_{14}O_8N_3P$ , prisms, decomp.  $230-233^\circ$  (corr.), slow heating.  $[\alpha]_D^{50} + 40.0^\circ$  to  $+48.5^\circ$  in water;  $[\alpha]_D^{25} + 26.0^\circ$  in 10% hydrochloric acid,  $+44.5^\circ$  in 5% ammonia,  $+25.5^\circ$  in 2% sodium hydroxide;  $[\alpha]_D^{20} + 1.0^\circ$  and  $-21.0^\circ$ , respectively, in 5 and 10% sodium hydroxide.

Uridinephosphoric acid,  $C_9H_{13}O_9N_2P$ , small bunches of needles, m. p.  $198.5^\circ$  (corr.; decomp.).  $[\alpha]_D^{20} + 9.5^\circ$  in water,  $+6.5^\circ$  in 2% sodium hydroxide, and  $-15.0^\circ$  in 5% sodium hydroxide.

Monooammonium salt of uridinephosphoric acid, fine, curved, felted needles, decomp.  $240^\circ$ .  $[\alpha]_D^{50} + 10.5^\circ$  in water;  $[\alpha]_D^{25} + 2.5^\circ$  in 10% hydrochloric acid,  $+14.0^\circ$  in 5% ammonia;  $[\alpha]_D^{20} + 1.5^\circ$ ,  $-16.0^\circ$ ,  $-26.0^\circ$ , respectively, in 2, 5, and 10% sodium hydroxide.

Adenosine has  $[\alpha]_D^{20} - 60.0^\circ$  in aqueous solution,  $-43.5^\circ$  in 10% hydrochloric acid,  $-68.5^\circ$  in 5% sodium hydroxide.

Uridine,  $[\alpha]_D^{20} + 4.0^\circ$  in water,  $+5.0^\circ$  in 10% hydrochloric acid,  $-6.0^\circ$  in 5% sodium hydroxide.

The changes in the optical rotation are probably due to several causes, amongst which tautomeric changes possibly play an important part. Adenosine and uridine show the same character of optical rotation as the corresponding nucleotides. J. C. D.

## The Theory of Gels. II. The Crystallisation of Gelatin.

SAMUEL CLEMENT BRADFORD (*Biochem. J.*, 1920, **14**, 91-93).—It has been previously shown (A., 1919, ii, 139) that the reversible gelation of the natural emulsoids is a crystallisation process resulting from the viscosity of these substances and from their very small diffusion constants, which greatly retard the crystallisation of the cooling sols, altering the accumulation of a large excess concentration. Hydrosols of "crystal" leaf gelatin of 0.5 and 0.3% were made, quickly heated to  $100^\circ$ , and filtered into thoroughly clean, covered crystallising dishes. A small amount of mercuric chloride was added to prevent bacterial growth, and the solutions were allowed to evaporate at the ordinary temperature. By this means, a precipitate, consisting of microscopic spherites  $0.25 \mu$  to  $0.28 \mu$  in diameter, was obtained. From these results, it cannot be doubted that gelatin crystallises from water exactly as indicated by von Weimarn's theory. J. C. D.

**Swelling of Gelatin in Hydrochloric Acid and Sodium Hydroxide.** DOROTHY JORDAN LLOYD (*Biochem. J.*, 1920, **14**, 147-170).—This paper furnishes further experimental support to

the theory which holds that gelatin is an amphoteric colloid, the neutral form of which is stable only at the isoelectric point ( $P_H$  4.6,  $20^\circ$ ). The molecular weight is 10,000 or some multiple of 10,000. This neutral gelatin is only slightly soluble in hot water, and is insoluble in cold water. It may, however, combine with water to form complexes, perhaps of the nature of hydrates or solid solutions. On the acid side of  $P_H$  4.6, gelatin functions as a multi-acid base, giving rise to ionisable hydrochlorides, and at  $P_H$  2.5 practically all the protein exists in the form of such salt. At lower hydrogen-ion concentrations than that of the isoelectric point, gelatin acts as a polybasic acid, forming ionisable gelatinates with bases such as sodium. The reaction with hydrochloric acid is reversible, that with sodium hydroxide irreversible. The formation of keto-salts in acids and enol salts in alkalis is postulated.

Regarding gels, the author is of the opinion that they are two-phase structures consisting of a solid framework of precipitated neutral gelatin, with which is combined a certain amount of water, and an interstitial fluid which is a solution of gelatin salt. The volume of any system in the gel condition is determined by two opposing sets of forces, the elastic forces of the solid framework, which tend to make the volume contract, and the osmotic forces of the ionised gelatin salts dissolved in the interstitial fluid, which tend to make the volume expand. Hence neutral gelatin, being only one phase, cannot make a stable gel, but will make a gel which will be free to contract. Similarly, since the salt form of gelatin is a single phase, such cannot form a gel. Gelatin in this form will only form sols with water.

The volume occupied by a gelatin gel swelling in a fluid medium depends on the ratio of the mass of the dissolved electrolyte to the mass of gelatin, on the geometrical form of the gel, and also on the hydrogen-ion concentration of the medium. Gels which are swelling in a weakly acid or alkaline medium lose water on being transferred to an atmosphere of saturated vapour. The amount of water lost is a function of the reaction of the previous external fluid. This loss follows from the elastic properties of the gel, and is shown to be in accordance with the membrane theory of Donnan. Van Bemmelen's theory that the surface of a gel is to be regarded as a solid membrane perforated by pores is confirmed by observation.

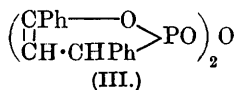
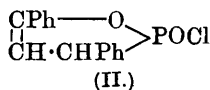
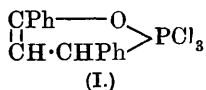
J. C. D.

**Chemical Kinetics of Catalase. I. Catalase from *Phyl. mit.*, Riv.** EIICHI YAMASAKI (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, 9, 13—58. Compare this vol., i, 194).—The velocity of decomposition of hydrogen peroxide by means of the catalase from *Phyllostachys mitis*, Riv., has been investigated at  $0^\circ$ ,  $10^\circ$ ,  $12.5^\circ$ ,  $18^\circ$ , and  $25^\circ$ . The catalase is obtained by crushing an edible sprout from a species of bamboo with water saturated with toluene. It was observed that the activity of the catalase steadily decreased during the reaction. The velocity of the reaction is represented by the equations  $-dC/dt = kEC$  and  $-dE/dt = -k'/k \cdot dC/dt = k'EC$ , where  $E$  and  $C$  are the concentration of the enzyme and

hydrogen peroxide respectively, and  $k$  and  $k'$  the reaction constants. The decrease of activity of the catalase is caused by the substrate and the product of the reaction, and its rate is approximately proportional to the principal reaction. The decrease of activity cannot be attributed to the change of the concentration of hydrogen ions produced by the decomposition of hydrogen peroxide, because a similar decrease of activity also occurs in acid solutions where the hydrogen-ion concentration is constant. The relative activity of the enzyme is always proportional to its concentration if the concentration of the hydrogen ion is maintained throughout the experiment. In a very dilute solution of hydrogen peroxide and a relatively concentrated solution of the enzyme, the activity increases in the first stage and then decreases. This may probably be explained by the following: (i) The ordinary reaction would be carried out at a rate somewhat higher than that calculated for a first-order reaction. (ii) The rate is decreased by oxygen and hydrogen peroxide in ordinary cases. (iii) Such effects are observed only in the course of reactions in very dilute solutions, because the concentrations of both the substrate and the product are very small, that is, the velocity constant has a maximum value. (iv) The retardation occurs with a measurable velocity, which is approximately proportional to the principal reaction. This explanation is in keeping with the observations of Waentig and Steche (A., 1913, i, 304) for solutions which were rapidly stirred in a vacuum.

J. F. S.

**A New Type of Addition Reaction.** JAMES B. CONANT and ALAN A. COOK (*J. Amer. Chem. Soc.*, 1920, **42**, 830—840. Compare A., 1918, i, 74).—The formation of ketophosphinic acids by the interaction of  $\alpha\beta$ -unsaturated ketones and phosphorus trichloride in presence of acetic acid is complete before the addition of water to the mixture, since the acid may be precipitated by the addition of benzene; acetyl chloride is the other product of the reaction. The first stage in the reaction with phenyl styryl ketone probably consists in the formation of the compound (I), since if acetic anhydride be used at the ordinary temperature in place of acetic acid, a mixture is produced of the acid chloride (II), a light-coloured, viscid oil, with an amount of the anhydride (III) which increases with the quantity of acetic anhydride employed. Water readily converts these compounds into  $\beta$ -benzoyl- $\alpha$ -phenylethyl-



phosphinic acid, and they combine with bromine to give products, from which, by decomposition with water,  $\beta$ -bromo- $\beta$ -benzoyl- $\alpha$ -phenylethylphosphinic acid,  $\text{COPh} \cdot \text{CHBr} \cdot \text{CHPh} \cdot \text{PO}(\text{OH})_2$ , m. p.  $196^\circ$ , is produced. This compound may also be prepared by bromination of  $\beta$ -benzoyl- $\alpha$ -phenylethylphosphinic acid. It is at once converted by sodium hydrogen carbonate, sodium carbonate, or sodium hydroxide into phenyl styryl ketone, sodium bromide,

and sodium phosphate. Its *monophenyl* ester, m. p. 179°, was produced by the action of phenol on the crude chloride obtained by treating with thionyl chloride either the acid or the product of the condensation of phenyl  $\alpha$ -bromostyryl ketone with phosphorus trichloride and acetic acid; it is best prepared by brominating *phenyl  $\beta$ -benzoyl- $\alpha$ -phenylethylphosphinate*, m. p. 146°, which is obtained from the corresponding acid through the chloride. *Diphenyl  $\beta$ -benzoyl- $\alpha$ -phenylethylphosphinate*, m. p. 125°, results in small quantities in the preparation of the monophenyl ester, but is best obtained by treating the acid with two molecular proportions of thionyl chloride, and subsequently with phenol. It dissolves in cold sodium ethoxide solution, and is converted into the monophenyl ester. The monophenyl ester is also obtained by treating the mixture of the compounds (II) and (III) with phenol. It is accompanied by the compound,  $\begin{array}{c} \text{CPh} \text{---} \text{O} \\ | \\ \text{CH} \cdot \text{CHPh} \end{array} > \text{PO} \cdot \text{OPh}$ , an oil insoluble in cold aqueous alkali, but convertible into the monophenyl ester either by solution in alcoholic sodium hydroxide solution or by treatment first with hydrogen chloride at 125° and then with water. J. K.

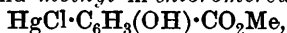
**Improved Method for the Preparation of Primary Arsanilic Acid.** HAROLD C. CHEETHAM and JOHN H. SCHMIDT (*J. Amer. Chem. Soc.*, 1920, **42**, 828—829).—Fichter and Elkind's process for the preparation of arsanilic acid (A., 1916, i, 444) gives only a fair yield, but better than that of Kober (A., 1919, i, 182). It was found best to heat a mixture of dry arsenic acid ( $\frac{1}{2}$  gram-mol.) with aniline ( $\frac{5}{3}$  gram-mol.) for twelve hours at 150—160°, the yield of purified product being 26%. J. K.

**Aromatic Mercuridicarboxylic Esters.** WALTER SCHOELLER, WALTER SCHRAUTH, and RICHARD HUETER (*Ber.*, 1920, **53**, [B], 634—643).—The non-toxicity of mercuridipropionic acid and mercuridibenzoic acid in comparison with the highly toxic mercury diaryls or dialkyls has been shown by Müller, Schrauth, and Schoeller (A., 1911, ii, 755) to be attributable to the excretion of the former unchanged from the organism in which the latter are decomposed. The present investigation deals with the production of mercuridicarboxylic acids, which would be more readily decomposed, and of their derivatives, which would not be eliminated, the ultimate object being an examination of their toxicity, the results of which are described elsewhere.

*Methyl o-chloromercuribenzoate*,  $\text{HgCl} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$ , needles, m. p. 162° after softening at 142°. is prepared by heating methyl benzoate, mercury acetate, and glacial acetic acid, separation of the methyl di- and mono-*o*-acetoxymmercuribenzoates by means of acetone, and treatment of a solution of the latter in aqueous alcohol with sodium chloride solution. It is converted by hydrogen

sulphide in methyl-alcoholic solution into *methyl sulphidodimercurio-benzoate*,  $S(Hg \cdot C_6H_4 \cdot CO_2Me)_2$ , white, amorphous powder, which softens and gradually darkens when heated; the latter is transformed at  $120^\circ$  into *methyl mercuridi-o-benzoate*, colourless crystals, which is hydrolysed by *N*-sodium hydroxide solution to mercuridi-benzoic acid, identical with the product prepared by Pesci in another manner.

*Methyl acetoxymercurisalicylate*, m. p.  $202^\circ$  (corr.) after slight previous softening, and *methyl m-chloromercurisalicylate*,



are prepared in the same manner as the corresponding benzoates, and are similarly transformed into *methyl sulphidodimercurisalicylate*, white, amorphous powder, and *methyl mercuridisalicylate*, m. p.  $178-180^\circ$  (corr.). *Ethyl acetoxymercurisalicylate*, needles, grouped in clusters, m. p.  $206^\circ$  (corr.) after softening at  $200^\circ$ , is converted by saturated aqueous sodium thiosulphate solution into *ethyl mercuridisalicylate*, m. p.  $193^\circ$  (corr.).

*Methyl mercuridianthranilate* forms small, yellow needles, m. p.  $196-197^\circ$  (corr.) after slight previous decoloration, whilst *methyl mercuridi-p-aminobenzoate* crystallises in yellow needles, m. p.  $176^\circ$  (corr.).

H. W.

**Phenylthiolmercuri-chloride.** H. LECHER (*Ber.*, 1920, 53, [B]. 568—577).—In continuation of previous investigations (A., 1916, i, 41), the author has endeavoured to prepare a mixed mercaptide of the type  $R'S \cdot Hg \cdot SR''$ , and, for this purpose, has studied the action of phenylthiolmercuri-chloride,  $HgCl \cdot SPh$ , on sodium ethyl sulphide; reaction is found to proceed, for the greater part at any rate, in accordance with the equation  $2HgCl \cdot SPh + 2NaSEt = 2NaCl + Hg(SPh)_2 + Hg(SEt)_2$ , although the complete absence of the mixed mercaptide is not definitely proved. The possibility that the chloride should be formulated  $Hg(SPh)_2 \cdot HgCl_2$ , appeared to be discounted by determinations of the molecular weight in boiling ethyl acetate solution, which indicated the simple structure. The explanation of the course of the reaction is found in the observation that phenylthiolmercuri-chloride is dissociated in solution into mercury phenylmercaptide and mercuri-chloride,  $2HgCl \cdot SPh \rightleftharpoons Hg(SPh)_2 + HgCl_2$ . The chloride can be readily prepared by mixing solutions of equivalent amounts of mercury phenylmercaptide and mercuric chloride, and the latter can also be extracted from solutions of the mercuri-chloride in organic solvents by sodium chloride solution. Further, if a solution of phenylthiolmercuri-chloride in pyridine is treated with ammonia, mercuric chloride is precipitated, whilst mercury phenylmercaptide remains in solution.

Mercury phenylmercaptide has been shown to undergo partial dissociation when heated into phenyl disulphide and mercury (*loc. cit.*). It is now shown that phenylthiolmercuri-chloride behaves in an analogous manner; when heated, it exhibits thermochromism, and melts at  $191.5^\circ$ , dissociating for the greater part

into diphenyl disulphide and mercurous chloride. A small portion, however, always remains on decomposition, and, conversely, small amounts of phenylthiolmercuri-chloride can be obtained by heating a mixture of the disulphide and mercurous chloride. H. W.

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## Physiological Chemistry.

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### Variations in the Chemical Composition of Human Blood.

FREDERICK S. HAMMETT (*J. Biol. Chem.*, 1920, **41**, 599—615).—Whilst the total nitrogen, non-protein nitrogen, and sugar of the blood vary in the same person from week to week, there is a tendency for the level of these variations to be characteristically individual. There is no practical difference between the absolute amounts of the constituents in bloods taken fourteen hours after food and three and a-half hours after breakfast. The absolute amount of creatinine is constant for the individual and for the species. The variations of urea, uric acid, creatine, and other non-protein nitrogenous substances are discussed. J. C. D.

**Anti-coagulating and Hæmolysing Action of Sodium Nucleate. Action on Brewer's Yeast.** DOYON (*Compt. rend.*, 1920, **170**, 966—967).—Sodium nucleate used in the form of a powder possesses an anti-coagulating power and exerts a very energetic hæmolysing action. It also prevents the decomposition of sugar into alcohol and carbon dioxide by brewer's yeast.

W. G.

**Effect of Alkali Fluorides on Digestion.** GROSSERON (*Ann. Chim. anal.*, 1920, [ii], **2**, 111).—According to some investigators, sodium fluoride has no action on the ordinary digestive process, but inhibits lactic, butyric, and acetic fermentation. It is suggested that the use of the salt as a preservative for butter should be permitted.

W. P. S.

**Effect of Intravenous Injections of Active Deposit of Radium on Metabolism in the Dog.** RUTH C. THEIS and HALSEY J. BAGG (*J. Biol. Chem.*, 1920, **41**, 525—535).—The injection was followed by an increased excretion of nitrogen, which reached a maximum figure on the second day after treatment. Urea fluctuated with total nitrogen, but there was a definite increase in excretion of ammonia and uric acid.

J. C. D.

**Nutritive Factors in Plant Tissues. IV. Fat-soluble Vitamine.** THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1920, **41**, 549—565).—Rats

which received 0.1 gram of butter daily showed considerable ability to grow, whilst 0.5 gram per day is sufficient to restore to good nutritive condition and growth rats declining on diets deficient in the fat-soluble accessory substance. In comparison with these values, it is shown that 0.1 gram of dried tomato daily will supply all the fat-soluble factor for normal growth. Of other vegetables tested, cabbage was the least satisfactory, whereas 0.1 gram of dried lucerne, clover, timothy grass, and spinach will furnish at least as much of the vitamine as the same weight of butter.

The thermostability of the fat-soluble growth factor is discussed, and the observations of Steenbock, Boutwell, and Kent (A., 1918, i, 513) and of Drummond are not confirmed (A., 1919, i, 363).

J. C. D.

**Relation between the Total Acidity, the Concentration of the Hydrogen Ion, and the Taste of Acid Solutions.** R. B. HARVEY (*J. Amer. Chem. Soc.*, 1920, **42**, 712—714).—The sourness of fruit and fruit juices is shown to depend both on the hydrogen-ion concentration and on the total free acid contained in the juice. The tendency to produce hyperacidity in the ingestion of fruits is dependent on the total quantity of acid ingested, and not necessarily on the hydrogen-ion concentration alone. The addition of sugar does not affect this tendency, which, although it changes the taste, does not affect either the total acidity or the hydrogen-ion concentration.

J. F. S.

**The Formation of Ferrous Sulphide in Eggs during Cooking.** CHARLES KENNETH TINKLER and MARION CROSSLAND SOAR. (*Biochem. J.*, 1920, **14**, 114—119).—The discoloration on the surface of the yolk of a "hard-boiled" egg is due to the formation of ferrous sulphide, by the liberation of hydrogen sulphide from the decomposition of a sulphur compound of the egg-white and its action on the iron contained in the yolk.

J. C. D.

**A Pressor Compound from the Pituitary Gland.** ALBERT C. CRAWFORD (*J. Pharm. and Expt. Ther.*, 1920, **15**, 81—94).—The paper opens with a review of the literature on the active principles of the pituitary gland. The pressor substance is not extracted from the dried, powdered posterior lobes by alcohol, but is extracted by acidified alcohol. From this extract, anhydrous ether precipitates the compound as a white or slightly coloured amorphous product, which is readily soluble in water.

The fractionation of extracts prepared from the posterior lobes is described, and the preparation of a highly active pressor substance, which is precipitated by soluble mercury and silver salts, is described. No crystalline derivatives have yet been obtained.

J. C. D.

**Zinc in the Human Organism.** SINICHA GIAYA (*Compt. rend.*, 1920, **170**, 906—909).—The examination of the viscera of a number of corpses shows the invariable presence of zinc, the proportion

increasing with age. Thus, the amounts found varied from 0.0009% in the case of a child three months old up to 0.005% in the case of a man seventy years old. The distribution of zinc in the different organs corresponds with the following descending order: brain, lungs, stomach, liver, kidneys, intestine, heart, and spleen. W. G.

**A Case of Adipocere.** G. FLORENCE (*Bull. Soc. chim. biol.*, 1919, 1, 185—188).—A sample of adipocere gave negative tests for calcium. After removal of the fatty substances by extraction with ether, the residue contained 11.3% of nitrogen, and gave no reaction with Millon's reagent or Hopkins and Cole's reagent. It is therefore thought to be of the nature of collagen, which had escaped the transformation into fat. The author discusses the possibility of straight-chain polypeptides being converted into fatty acids, such as stearic acid, by a process of deamination and reduction.

J. C. D.

**Milk as a Source of Water-soluble Vitamine. II.** THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1920, 41, 515—523).—The authors have been unable to confirm in detail the classical experiments of Hopkins (A., 1912, ii, 779). They find that a much larger quantity of milk than the 2 c.c. used by Hopkins is necessary to supply the vitamins required by the rat for normal growth. The discrepancy does not appear to be due to the diet of the cow from which the milk is obtained, or to the character of the inorganic constituents of the artificial ration.

J. C. D.

**The Presence of Amylase in Milk and Cheese.** MASAYOSHI SATO (*Biochem. J.*, 1920, 14, 120—130).—The presence of amylase in milk, already reported by many workers, is confirmed. It is also present in commercial Cheddar cheese, although in variable amounts. Certain differences in the digestibility of various forms of starch by amylase were noted.

J. C. D.

**Acidosis. XVI. The Titration of Organic Acids in Urine.** DONALD D. VAN SLYKE and W. W. PALMER (*J. Biol. Chem.*, 1920, 41, 567—585).—The organic acids present, both free and as salts, in urine are estimated by titrating between the hydrogen-ion concentrations represented by  $p_H$  8 and  $p_H$  2.7 respectively, after removal of phosphates and carbonates by means of calcium hydroxide. It appears that such titration represents between 95 and 100% of the organic acids present. It also includes weak bases, the dissociation constants of which fall within a range in the neighbourhood of  $10^{-11}$ , but of this class only creatinine, and at times creatine, appear to be present in significant amounts in human urine. The average twenty-four-hour excretion of organic acids in normal young men appears to be about 5.7 to 9.8 c.c. of 0.1N-acid (uncorrected for creatinine). There appears to be little difference in the rate of excretion during day and night.

Data from cases of methyl alcohol poisoning and diabetes are examples of acidosis due to organic acids of different types. In the first case, a part of the total organic acid excretion was due to formic, lactic, and hydroxybutyric acids, but the greater part to acids of unknown nature. In diabetes, the rise in the excretion of acetone substances is so accurately paralleled by the rise in titrated organic acids that it is probable (1) that organic acids other than the acetone substances are not excreted in significant amounts in diabetic acidosis, and (2) that the easily performed organic acid titration may be used for approximate estimation of the acetone substances in diabetic urine.

J. C. D.

### **The Anti-scorbutic Properties of Concentrated Fruit Juices.**

III. ARTHUR HARDEN and ROBERT ROBISON (*Biochem. J.*, 1920, **14**, 171—177).—The anti-scorbutic property of orange juice is not appreciably destroyed by evaporation to dryness under suitable conditions.

The dry residue retains considerable activity after storage for two years in a dry atmosphere at the ordinary temperature.

J. C. D.

**Effect of Heat on the Anti-scorbutic Accessory Factor of Vegetable and Fruit Juices.** ELLEN MARION DELF (*Biochem. J.*, 1920, **14**, 211—228).—When cabbage, swede, and orange juices are subjected to temperatures up to 130°, a corresponding reduction of their anti-scorbutic properties occurs. The destruction is most marked in the case of cabbage juice, and least in the case of orange juice. The greater stability of orange juice to heat is maintained even when the juice is nearly neutralised before heating. There is evidence that growth may be affected by the limitation of the anti-scorbutic element in the diet, apart from the appearance of definite symptoms of scurvy and apart from deficiency in the other growth-promoting accessory factors.

The unexpected stability of swede and orange juice at temperatures above 100°, when the heating is conducted in the absence of air, may perhaps indicate that destruction of the anti-scorbutic factor is an oxidation process. This observation naturally has an important bearing on the canning and preserving of fruits and vegetables.

J. C. D.

**Physiological Action of Fumes of Iodine.** A. B. LUCKHARDT, F. C. KOCH, W. F. SCHROEDER, and A. H. WEILAND (*J. Pharm. Expt. Ther.*, 1920, **15**, 1—21).—Iodine fumes may be absorbed from the human skin and appear in the urine. Iodine absorbed in this manner may actually increase the iodine content of the thyroid gland and induce a pronounced change in the histological features of that gland. The inhalation of small quantities of iodine fumes produces similar results, but larger doses may lead to respiratory disturbances and fatal acute pulmonary oedema. The administration of iodine by such inhalation is regarded as a dangerous procedure.

J. C. D.

**The Formation of Acetone Substances following Ether Anæsthesia and their Relation to the Plasma Bicarbonate.**

JAMES J. SHORT (*J. Biol. Chem.*, 1920, **41**, 503—513).—A study of the acetoacetic acid, acetone, and  $\beta$ -hydroxybutyric acid of the blood was made before and after ether anæsthesia in order to ascertain whether the formation of these substances was in any way responsible for the fall in alkaline reserve which accompanies that condition. Apparently the so-called acetone substances are not formed promptly enough during ether anæsthesia to account for the decrease in plasma bicarbonate. The analytical methods for the acetone substances (Van Slyke and Fitz, A., 1919, ii, 436) may be rendered less accurate by the presence of fat and ether, or ether alone. J. C. D.

**The Minimum Concentration of  $\beta\beta'$ -Dichloroethyl Sulphide (Mustard Gas) Effective for the Eyes of Man.**

C. I. REED (*J. Pharm. Expt. Ther.*, 1920, **15**, 77—80).—Concentrations of 0.0005 mg. per litre of mustard gas will produce visible reactions in less than one hour of exposure in the eyes of individuals whose cutaneous resistance is relatively high. J. C. D.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Action of *Bacillus fluorescens liquefaciens* (Flügge) on certain Amino-acids.** A. BLANCHETIÈRE (*Bull. Soc. chim. biol.*, 1920, **2**, 29—36. Compare A., 1916, i, 699).—The amino-acids are able to act as the sole source of carbon and nitrogen for the development of this organism. The rates and degree of attack are very variable, histidine, alanine, and asparagine being particularly suitable for utilisation. Substitution of an amino-group by benzoylation appears to oppose the utilisation of the amino-acid, an observation which is in agreement with the accepted theories on the decomposition of amino-acids by bacteria. The benzoyl derivatives are decomposed.

J. C. D.

**Influence of Reaction on Colour Changes in Tyrosine Solutions.** (MRS.) ELFRIDA CONSTANCE VICTORIA VENN (*Biochem. J.*, 1920, **14**, 98—102).—Cornish and Williams showed (A., 1917, i, 613) that certain groups of bacteria isolated from discoloured Stilton cheeses are capable of producing changes of colour in media containing suspensions of caseinogen and certain amino-acids. It was found that the reaction of the media on which the organisms were grown exercised a powerful influence on the degree of discoloration. It is now shown that there is a definite range of reaction over which the organism studied is capable of producing a dis-

coloration in tyrosine solutions. A modified form of hydrogen electrode is described, which presents several advantages over many types now in use. J. C. D.

**Comparative Studies on Respiration. X. Toxic and Antagonistic Effects of Magnesium in Relation to the Respiration of *Bacillus subtilis*.** MATILDA MOLDENHAUER BROOKS (*J. Gen. Physiol.*, 1920, 2, 331—336).—Magnesium chloride in concentrations below 0.01M has little effect on the rate of respiration of *B. subtilis*; at 0.03M there is an increase in the rate, whilst in the higher concentrations there is a gradual decrease. There is a marked antagonism between magnesium and sodium chlorides, and a very slight antagonism between the chlorides of magnesium and calcium. J. C. D.

**The Fats of Tubercle Bacilli.** H. AGULHON and A. FROUIN (*Bull. Soc. chim. biol.*, 1919, 1, 176—184).—Large amounts of fatty substances may be extracted from dried tubercle bacilli by alcohol. This material is composed of fatty acids, neutral fats, esters of the higher alcohols, hydrocarbons, and a substance containing phosphorus. The latter represents about 14% of the total alcoholic extract of the organisms, and is composed of a mixture of substances of phosphatide character, which on hydrolysis yields fatty acids, glycerol, a base analogous to choline, and a gummy substance which yields dextrose. The presence of cholesterol in the extracts of the bacilli was not established. J. C. D.

**Production of Formic Acid by Yeasts in Media containing Amides.** P. THOMAS (*Ann. Inst. Pasteur*, 1920, 34, 162—176. Compare this vol., i, 126).—The volatile acidity produced during the culture of yeast on media containing acetamide is in part due to the formation of formic acid and in part due to the formation of acetic acid, the relative proportions of these two acids varying with the conditions. The presence, in addition, of various ammonium salts has a very marked effect on the total volatile acidity and the relative amounts of the two acids produced. In the presence of ammonium sulphate, oxalate, succinate or hydrogen carbonate the volatile acid produced is almost entirely formic acid, whilst in the presence of ammonium aspartate the two acids are produced in almost equal amounts.

The author discusses the various theories put forward to explain the formation of acetic acid, and concludes that the mechanism is not a simple one, but that there are several phenomena, which will function according to the conditions and may replace or superpose on one another, as the conditions vary. W. G.

**Alteration in the Inverting Power of Top Yeast by Pre-treatment.** STURE LÖVGREN (*Fermentforsch.*, 1920, 3, 221—240; from *Chem. Zentr.*, 1920, i, 473—474).—The experiments were undertaken with the object of determining the influence of the inorganic constituents on the formation of saccharase and

the differences between their action on bottom yeast, which has generally been used previously by Euler and his co-workers, and on top yeast. Pre-treatment of the yeast was effected with sugar, ammonium acetate, magnesium chloride or sulphate, calcium chloride, potassium chloride, sodium chloride, potassium dihydrogen phosphate, yeast water, alcohol, acetone, or carbamide, sometimes singly and sometimes in combinations. The results are summarised in the following statements: (1) The neutral salts investigated do not appear to have any actual influence on the variation of the inverting power of the types of top yeast used, either in small amounts at the ordinary temperature or in larger quantities at the ordinary or higher temperature. (2) Certain experiments indicate that the inverting power of top yeast may be distinctly increased by suitable pre-treatment. Addition of nitrogenous nutriment is advantageous, but not essential. In the first twenty-four hours (of fermentation) the inverting power increases slowly or may even decrease; after cessation of fermentation, it increases gradually at first, then more rapidly to a maximum, at which it remains for a time, and then slowly decreases again. The curves are more or less flattened according to the properties of the original yeast. (3) One experiment shows that top yeast is much less suitable for enrichment experiments of this kind than bottom yeast. (4) The inversion constants of the original yeasts varied between 20 and 40, with a mean value (from nine estimations) of 28 per gram of yeast (30% dry substance) and 9.6 grams of sucrose at 16°, from which the constant  $3 \times 10^{-12}$  is calculated. (5) If the increase of inverting power is considered to be a consequence of augmented vitality due to the pre-treatment, the nitrogen nutriment must be regarded as essential. The fact that a marked increase can occur without administration of nitrogen is probably explained by the formation of the necessary amount of the latter by autolysis. H. W.

**Activation of Living Yeast by Yeast Extract and by Salts of Organic Acids.** HANS VON EULER (*Zeitsch. techn. Biol.*, 1919, 7, 155—164; from *Chem. Zentr.*, 1920, i, 473).—I. *Activation of Living Yeast by Yeast Extract or Preparations of Yeast Extract.*—In connexion with the investigations of Euler and Berggren (A., 1913, i, 145) and Harden and Young (A., 1914, i, 237), the author adduces new evidence to show that alcoholic fermentation by fresh top-yeast is greatly accelerated by activators, presumably co-enzymes, which are present in aqueous yeast extract, and that the phenomenon is observed when the number of cells in the fermenting liquor undergoes no, or very slight, increase. The activation of dry yeast by the co-enzyme is almost independent of the acidity of the solution in the region  $P_H=3-7$ .

II. *Activation of Living Yeast by Salts of Organic Acids.*—In contrast to Harden and Young, the author finds that the increase in the number of cells due to the addition of alkali formate never exceeds the experimental error involved in counting. On the other hand, it is shown that alcoholic fermentation by fresh top-yeast is greatly accelerated by ammonium or alkali formate. H. W.



**Regeneration of Saccharase in Pre-treated Yeast.** HANS VON EULER and OLOF SVANBERG (*Zeitsch. techn. Biol.*, 1919, 7, 165—172; from *Chem. Zentr.*, 1920, i, 473).—The authors have investigated the length of period necessary for the re-formation of enzyme-content removed by previous treatment; the results so far obtained do not permit a definite conclusion to be drawn. H. W.

**Ferment Action. VI.** A. FODOR (*Fermentforsch.*, 1920, 3, 193—200; from *Chem. Zentr.*, 1920, i, 471—472. Compare Abderhalden and Fodor, A., 1919, i, 369).—An active colloidal mixture can be separated from yeast extract by the addition of twice its volume of absolute alcohol; the precipitate (*R*) is separated after twelve hours and thoroughly washed with alcohol. It is not completely dissolved by protracted treatment with water at 37°, but leaves a residue (*r*), which yields a clear, golden-yellow solution with dilute sodium hydroxide, from which it does not separate on treatment with excess of acid. Whilst *R* contains the colloids of yeast extract, the aqueous-alcoholic filtrate is free from them, and is completely inactive fermentatively. The aqueous extract from *R* is readily coagulated when heated and, when cautiously acidified, deposits a perfectly white precipitate. It causes the fission of glycyl-*l*-leucine, but its activity is small in comparison with that of the original yeast extract. The solution also contains magnesium and phosphoric acid ions and, when rendered alkaline with sodium hydroxide, gives a crystalline precipitate of magnesium sodium phosphate and some magnesium ammonium phosphate in the same manner as the original extract. The residue, *r*, consists mainly of denatured proteins which are precipitated when the solution in alkali is acidified (owing to the action of the salt). According to the nitrogen content, this product differs from that precipitated by acids from the aqueous extract of *R*, though each is to be regarded as a nucleoprotein.

If alcohol is added to the yeast extract after removal of phosphate by addition of alkali, a precipitate, *R*<sub>1</sub>, is obtained, which leaves a residue, *r*, after treatment with water. The faintly alkaline aqueous filtrate is not noticeably coagulated by heat even after neutralisation, yields at most an opalescence when cautiously acidified with hydrochloric acid, and is completely inactive towards glycyl-*l*-leucine even after addition of magnesium phosphate solution, the favourable influence of which on fermentative activity has been frequently demonstrated. The product, *r*<sub>1</sub>, closely resembles *r*, and has the same nitrogen content. In the dry condition neither can function as acid or base in the sense of the ionic theory, though each acquires this property after hydration and increase of surface, which slowly occurs under the influence of acid or alkali. If more concentrated alkali hydroxide is used in reprecipitation, elimination of phosphoric acid occurs, even to such an extent that the substance becomes free from phosphorus; the nitrogen content is simultaneously altered.

In connexion with the present and previous investigations, the development of ferment action is explained on a colloidal chemical

basis. The union of the ferment, a negatively charged colloid, by adsorption with the substrate, activates the elements necessary for the hydrolysis of the latter by bringing them into the ionic condition. This happens as a consequence of the partial diminution of the adsorption potential of the colloidal particles by the opposite charge of the substrate. The optimal hydrogen-ion concentration depends on the individual properties of the ferment colloids and the amphoteric substrate and their mutual relationships. In the case of ferments which are active in alkaline solution, this becomes more displaced towards the alkaline side as the difference in acidic nature between the colloid and the substrate increases. H. W.

**The Products of the "Acetone-*n*-Butyl Alcohol" Fermentation of Carbohydrate Material, with Special Reference to some of the Intermediate Substances Produced.**

JOSEPH REILLY, WILFRED JOHN HICKINBOTTOM, FRANCIS ROBERT HENLEY, and AAGE CHRISTIAN THAYSEN (*Biochem. J.*, 1920, **14**, 229—251).—In a normal fermentation of maize mash the acidity rises until a maximum is reached from thirteen to seventeen hours after inoculation. After this point is reached there is a very marked acceleration in the rate of production of acetone, *n*-butyl alcohol, carbon dioxide, and hydrogen, the acidity falling gradually to a constant value. The greater part of the acids produced are volatile in steam, and butyric and acetic acids were identified in the distillate. These acids are probably intermediate products in the production of acetone and butyl alcohol. Evidence in support of this is given by the results of carrying on the fermentation in the presence of calcium carbonate, when practically no acetone or butyl alcohol was obtained.

When acetic acid or ethyl acetoacetate is added to the fermenting mash an increased yield of acetone is obtained. Addition of formic acid and trichloroacetic acid appeared to inhibit fermentation, whilst propionic and butyric acids are converted into the corresponding alcohols.

A tentative suggestion of the action is put forward, in which acetic acid is considered as a monoketide,  $\text{H}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{OH}$ . By condensation  $\text{CH}_2\cdot\text{CO}$  yields  $\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{CO}$ , which by elimination of  $\text{CO}_2$  and the addition of the elements of water would yield acetone. Similarly, the increased yield of acetone from acetoacetic acid may be explained on the assumption that this substance possesses the structure of a diketide. This hypothesis may be extended and is capable of explaining ordinary alcoholic fermentation. No direct evidence was obtained of the formation of acetaldehyde or of formic acid as an intermediate product in the acetone fermentation.

J. C. D.

**Influence of a Reduced Amount of Potassium on the Physiological Characters of *Sterigmatocystis nigra* [*Aspergillus niger*].** M. MOLLIARD (*Compt. rend.*, 1920, **170**, 949—951).—When all but one-eightieth of the potassium phosphate

in the normal culture medium is replaced by sodium phosphate, the growth of *Aspergillus niger* is very slow and the yield of mycelium is very small. The sugar is to a large extent oxidised, but instead of giving almost entirely carbon dioxide, an important amount of oxalic acid is formed, the amount increasing regularly so long as there is any sugar left in the culture medium. Other points noted are the more rapid disappearance of the dextrose than of the levulose, the total absence of conidia and of the black pigment, formation of a golden-yellow pigment diffusing into the medium, and the production of a substance soluble in the culture solution and giving a blue colour with iodine.

W. G.

**The Utilisation of  $\alpha$ -Methylglucoside by *Aspergillus niger*.** ARTHUR W. DOX and G. W. ROARK, jun. (*J. Biol. Chem.*, 1920, **41**, 475—481).—*Aspergillus niger* grows very poorly on media containing  $\alpha$ -methylglucoside as the only source of carbon, but readily on sucrose media in the presence of the glucoside. More rapid utilisation of the glucoside occurs on the sucrose-free medium when the culture inoculated is a vigorous one, or one which has previously been growing in the presence of both sucrose and the glucoside. A gradual cumulative adaptation could not be demonstrated with certainty.

J. C. D.

**Synthesis of Aromatic Amino-acids in the Living Cell.** L. HUGOUNENQ and GABRIEL FLORENCE (*Bull. Soc. chim. biol.*, 1920, **2**, 13—18).—*Aspergillus niger* produces proteins containing the aromatic amino-acids when growing on culture media containing inorganic nitrogen, sucrose, and tartaric acid. It is possible that it is able to utilise the carbon chain of a pentose for these synthetic processes. Probably the products of assimilation are broken down into substances of small molecular dimensions before the synthetic processes are commenced, and a parallel is drawn with the metabolic and anabolic processes in the higher animals.

J. C. D.

**Photo-synthesis in Fresh-water Algæ. I. The Fixation of Both Carbon and Nitrogen from the Atmosphere to Form Organic Tissue by the Green Plant Cell. II. Nutrition and Growth Produced by High Gaseous Dilutions of Simple Organic Compounds, such as Formaldehyde and Methyl Alcohol. III. Nutrition and Growth by means of High Dilutions of Carbon Dioxide and Oxides of Nitrogen without Access to Atmosphere.** BENJAMIN MOORE and T. ARTHUR WEBSTER (*Proc. Roy. Soc.*, 1920, [*B*], **91**, 201—215).—Experimental evidence is given in support of the view that the lowest type of synthesising cell existing, namely, the unicellular alga, possesses the power of fixing carbon and nitrogen and building these up into reduced organic compounds with uptake of energy, the source of the energy being the sunlight. It is shown that formaldehyde or methyl alcohol fed to such a

cell at a sufficiently high dilution can be used as a nutrient source of carbon in absence of carbon dioxide, and very marked growths have been obtained with these substances as the sole source of carbon. In the absence of all other sources of nitrogen except the atmospheric nitrogen, but with abundance of carbon dioxide, the unicellular algæ can fix nitrogen, grow, and form proteins. The rate of fixation and growth is, however, greatly accelerated if nitrites or oxides of nitrogen are available, and the latter may be supplied in the gaseous form from the atmosphere. W. G.

**The Inhibition of Invertase in the Sap of *Galanthus nivalis*.** T. G. MASON (*Sci. Proc. Roy. Dubl. Soc.*, 1920, **16**, 83—97).—Experiments with the sap of the leaves of *Galanthus nivalis*, extracted under varying conditions, indicate that factors inhibiting the activity of the invertase may be present in the sap. Changes of a nature not yet clearly understood occur in the sap after its extraction from the leaf, which lead to a clumping of the colloids, and possibly the enzyme may be inactivated by adsorption on the coagulated colloids. W. G.

**Presence of Gentianose and Sucrose in various Gentians.** MARC BRIDEL (*J. Pharm. Chim.*, 1920, [vii], **21**, 306—311; *Bull. Soc. chim. biol.*, 1920, **2**, 37—41). Compare A., 1913, i. 149, 434, 690).—The author has detected the presence of both gentianose and sucrose in the roots of *Gentiana cruciata* and *G. purpurea*. The reversible change between gentianose and sucrose is governed by the activity of the enzyme gentiobiase. W. P. S.

**Anthocyanins. I. The Anthocyanins of the Young Leaves of the Grape Vine.** OTTO ROSENHEIM (*Biochem. J.*, 1920, **14**, 178—188).—The red pigment of the young leaves of the grape vine is probably identical with oenidin, the anthocyanidin derived from the pigment of the purple grape. This is the first case which has been noted in which the red pigment of the leaves is a free anthocyanidin, and the European species *Vitis vinifera* appears to be the only representative of the family *Vitis* which is so characterised. The occurrence of a colourless modification of the pigment was demonstrated, for which the general name *leucoanthocyanin* is proposed. It is present in combination possibly with carbohydrate, and is converted into anthocyanidin by strong acids. J. C. D.

**Distribution of Lycorine in the N.O. Amaryllidaceæ.** K. GORTER (*Bull. Jard. bot. Buitenzorg*, 1920, [iii], **1**, 352—358).—The first accurate description of an alkaloid of this order refers to lycorine from *Lycoris radiata*, Herb. (Morishima, A., 1899, i, 92), and this is identical with narcissine (Ewins, T., 1910, **97**, 2406) from *Narcissus pseudonarcissus*, L. (compare Asahina and Sugii, A., 1913, i, 1093). The latter name should therefore be abandoned; the formula of the alkaloid is  $C_{16}H_{17}O_4N$  (Ewins), with which the analytical results of Morishima agree better than with

the formula  $C_{32}H_{32}O_8N_2$  proposed by him, which is, moreover, excluded by molecular-weight determinations (Ewins, Asahina, and Sugii). The alkaloid of *Buphane disticha*, Herb. (Tutin, T., 1911, 99, 1240) is also lycorine, as is that in *Narcissus Tazetta*, L. (Yamanouchi, *Arch. Pharm.*, 1913, 251, 357). Gorter has further found lycorine in *Zephyranthes rosea*, Lindl., *Crinum asiaticum*, L., *C. giganteum*, Andr., *C. pratense*, Herb., *Hymenocallis littoralis*, Salisb., *Eucharis grandiflora*, Planch., and *Eurycles sylvestris*, Salisb. *Crinum* spp. contain most (0.1—0.18% of bulb). G. B.

**A New Plant containing Coumarin: *Melittis melissophyllum*, L.** P. GUÉRIN and A. GORIS (*Compt. rend.*, 1920, 170, 1067—1068).—The leaves of *Melittis melissophyllum*, L. contain coumarin apparently in the form of a glucoside decomposable by emulsin. The coumarin may be extracted along with quercetin from the dried leaves by 95% alcohol.

W. G.

**Constituents of *Morinda citrifolia*.** JOHN LIONEL SIMONSEN (T., 1920, 117, 561—564).

**Acidity and Acidimetry of Soils. I. Studies of the Hopkins and Pettit Method for Estimating Soil Acidity** HENRY G. KNIGHT (*J. Ind. Eng. Chem.*, 1920, 12, 340—344).—Investigation of this method (extraction with potassium nitrate solution and titration of the extract) showed that an acid soil gives the same acidity whether it is extracted with *N*/1-potassium nitrate, potassium chloride, sodium nitrate, sodium chloride, or calcium chloride solution. The acidity of the salt extract of an acid soil is independent of the temperature within the range of 25° to 90°, but the acidity of the first portions of the extract increases with increase of the concentration of the salt solution. The difference in absorption of calcium and potassium from solutions of their bases by an acid soil may be due to precipitation. There is a basic exchange when a salt solution is added to an acid soil; alumina is dissolved, but this does not account for the total acidity of the solution. Exchange of acid radicles is slight or does not occur.

W. P. S.

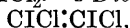
**Hysteresis of Aqueous Suspensions of Humus Earth.** HEINRICH PUCHNER (*Kolloid Zeitsch.*, 1920, 26, 159—168. Compare this vol., i, 274).—A continuation of the previously published work. The present paper deals particularly with hysteresis phenomena occurring in the insoluble portion obtained from the settling of suspensions of peat in water. It is shown that the delayed effects observed are due, not only to physical and chemical processes, but are very largely influenced by the growth of low forms of plant life.

J. F. S.

## Organic Chemistry.

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**Positive Halogen in Organic Compounds. Iodine in Di-iodoacetylene and Chloriodoethylene.** LLOYD B. HOWELL [with WILLIAM A. NOYES] (*J. Amer. Chem. Soc.*, 1920, **42**, 991—1010).—It is suggested that the reactivity of halogen substitution derivatives of acetylene is due to the quadrivalence of the carbon atom rather than to the presence of a bivalent carbon atom (Nef, A., 1898, i, 102), and also to the positive character of the halogen atom, also exemplified when halogen replaces hydrogen in amino-, imino-, or hydroxyl groups. In agreement with this, di-iodoacetylene is shown to be produced by the action of iodine monochloride on calcium carbide or copper acetylide, although acetylene itself gives  $\alpha$ -chloro- $\beta$ -iodoethylene (Plimpton, T., 1882, 392). Further, di-iodoacetylene is decomposed by neutral, more quickly by acid, solutions of potassium iodide, with formation of acetylene, iodine, and potassium hydroxide. Although nitrogen iodide is considered to contain positive iodine atoms (Chattaway, A., 1900, ii, 722), it could not be obtained from di-iodoacetylene by means of ammonia, but this is not surprising, since acetylene is iodinated by the iodide (Datta and Prosad, A., 1917, i, 332). The formation of hexachloroethane by the action of chlorine on di-iodoethylene (Biltz, A., 1897, i, 389) is preceded by the production of the very unstable compound,  $C_2Cl_4I_2$ , yellow needles, which apparently melt, but probably decompose, at  $42-43^\circ$ . It decomposes in the dark, even at temperatures below  $0^\circ$ , within a few minutes, giving *as*-dichlorodi-iodoethylene, iodine trichloride, and traces of a liquid, b. p.  $80-84^\circ/32$  mm., probably trichloriodoethylene. This result, the formation of di-iodoacetylene by the action of alcoholic potash, and the fact that the whole of the iodine is not converted into iodide by treatment with lime or sodium peroxide, indicate that the compound is  $\alpha\beta$ -dichloro- $\beta$ -iodoethylene  $\alpha$ -iododichloride,  $ClCl:CCl:ICl_2$ . *s*-Dichlorodi-iodoethylene,



is an odourless, pale yellow liquid, b. p.  $127.5-128.5^\circ/25-26$  mm., or  $243.5^\circ$  (corr. decomp.)/760 mm., which solidifies slightly below  $0^\circ$ . It reacts with difficulty with hot alcoholic silver nitrate solution, and gives di-iodoacetylene when treated with alcoholic potash. With chlorine, it gives an *iododichloride*,  $ClCl:CCl:ICl_2$ , a yellow compound, which liberates one molecular proportion of iodine from potassium iodide. The course of the chlorination of di-iodoacetylene is therefore represented as follows:  $C_2I_2 \rightarrow [Cl:C:ICl_2] \rightarrow ClCl:ClCl \rightarrow ClCl:CCl:ICl_2 \rightarrow [ClCl_2 \cdot ClCl_2] \rightarrow C_2Cl_6 + 2ICl \rightarrow 2ICl_3$ .  $\alpha$ -Chloroethylene  $\beta$ -iododichloride is produced by passing acetylene through a solution of iodine trichloride in hydrochloric acid; freshly crystallised from methyl alcohol, it melted at

66° (decomp.), but after several hours at 80°. Contrary to the statement of Thiele and Haakh (A., 1909, i, 865), its decomposition does not result in the formation of chlorine, but of iodine, iodine monochloride, and a number of liquid halogen compounds, of which the chief is  $\alpha\beta\beta$ -trichloro- $\alpha$ -iodoethane; no trace of *as*-chloriodoethylene could be discovered. Iodine trichloride as usually prepared contains a large quantity of the monochloride. A very satisfactory method of preparing solutions of the trichloride in hydrochloric acid consists in the addition of a finely ground mixture of iodic acid (3 mols.) and re-sublimed iodine (1 mol.) to a cooled solution of twice the theoretical volume of hydrochloric acid (D 1.19). Such solutions may be kept indefinitely, even at 30°. The positive character of the iodine atom in nitrogen tri-iodide is illustrated by the formation of iodine monochloride on addition of concentrated hydrochloric acid to the tri-iodide. J. K.

**Vapour Composition of Mixtures of Ethyl Alcohol and Water.** W. K. LEWIS (*J. Ind. Eng. Chem.*, 1920, 12, 496—499).—The vapour composition of mixtures of ethyl alcohol and water was determined by Vrevski (A., 1912, ii, 1139) under varying pressures at 40°, 55°, and 75°. These results have been recalculated and extended by extrapolation up to the boiling points of the liquids. The vapour composition curve is shown diagrammatically, whilst the change in the vapour composition with the alteration in the boiling point has been determined from the slope of the temperature curves and plotted in a diagram, so as to be applicable to pressures other than the atmospheric pressure. The total pressure exerted by a given mixture of ethyl alcohol and water at a given temperature, divided by the pressure of pure water at the same temperature, forms a ratio which changes but little with a change in the temperature. The value of this ratio rises rapidly from water (as unity) with each increase of alcohol to about 2.3 for pure ethyl alcohol. The value of this ratio at the boiling point is plotted as a separate curve to enable the relationship between pressure and temperature to be made under other conditions than atmospheric pressure, as, for example, in the lower part of a rectifying column. C. A. M.

**The Ceryl Alcohol and Cerotic Acid of Chinese Wax.** ALBERT GASCARD (*Compt. rend.*, 1920, 170, 1326—1328).—Ceryl cerotate, as isolated from Chinese wax and carefully purified, has m. p. 84°. When hydrolysed, the ceryl alcohol obtained therefrom has m. p. 80°, and gives an iodide, m. p. 59°. Analysis of the iodide and the behaviour of the iodide when treated with sodium amalgam confirm Brodie's formula,  $C_{27}H_{55}\cdot OH$ , for this alcohol. Similarly, the cerotic acid, m. p. 82—82.5°, isolated from the products of hydrolysis, is shown to have the formula  $C_{26}H_{53}\cdot CO_2H$ . W. G.

**Catalytic Preparation by the Dry Way of certain Ethers.** ALPH. MAILHE and F. DE GODON (*Bull. Soc. chim.*, 1920, [iv], 27, 328—330. Compare this vol., i, 6, 284).—When allyl alcohol

vapour is passed over calcined alum at 185—190°, a 30% yield of allyl ether is obtained. When the allyl alcohol is mixed with methyl alcohol or its four higher homologues, a certain amount of the mixed ethers is obtained, but the main product is allyl ether; in no case, however, is any appreciable amount of methyl ether or its homologues obtained. Under similar conditions, benzyl alcohol did not give benzyl ether, but a yellow, resinous compound,  $(C_7H_8)_n$ , but when the benzyl alcohol was mixed with methyl or ethyl alcohol, some mixed ether resulted. W. G.

**Decomposition of Nitric Esters.** ROBERT CROSBIE FARMER (T., 1920, 117, 806—818).

**The History of Zeise's Mercaptan and its Name.** O. ZEISE (*J. pr. Chem.*, 1919, [ii], 100, 48).—A personal note arising from Diergart's recent communication (this vol., i, 137) under the above title. H. W.

**Crystallographic Properties of Sulphonal.** H. SEIFERT (*Centr. Min.*, 1920, 97—101).—Sulphonal (diethylsulphondimethylmethane),  $CMe_2(SO_2Et)_2$ , crystallises in the monoclinic system, and is pseudo-rhombic in character;  $a:b:c=1.563:1:1.446$ ,  $\beta=90^\circ 31\frac{1}{2}'$ . Crystals were examined grown from water, aqueous alcohol, ether, ethyl acetate, chloroform, carbon tetrachloride, and toluene; the habit of the crystals varies considerably according to the solvent from which they are grown. The crystals are generally well developed polyhedra, but from toluene or alcohol skeleton crystals are frequently obtained. Striations and vicinal faces sometimes appear. There is a good cleavage parallel to  $a\{100\}$ , and the crystals show considerable plasticity. They are colourless and show negative double refraction, the optic axial plane being  $b\{010\}$ . E. H. R.

***n*-Butyl Chloroformate and its Derivatives.** FREDERICK DANIEL CHATTAWAY and EDOUARD SAERENS (T., 1920, 117, 708—711).

**The Use of  $\alpha\beta$ -Dichlorovinyl Ethyl Ether for the Production of Chloroacetates and Acid Chlorides.** HOLLAND CROMPTON and PAULE LAURE VANDERSTICHELE (T., 1920, 117, 691—693).

**Leucic [ $\alpha$ -Hydroxyisohexoic] Acid and Walden's Inversion of Leucic Acid.** SHINTARO KODAMA (*J. Tokyo Chem. Soc.*, 1919, 40, 825—862).—Certain amino-acids, for example, glutamic acid and its salts, are extensively used in Japan as taste-promoting substances in food. The author has obtained very sweet substances by de-aminising leucine. Crude leucine hydrochloride, prepared by the hydrolysis of protein, is dissolved in several volumes of water and de-aminised; calcium oxide precipitates crude calcium  $\alpha$ -hydroxyisohexoate, which is suspended in water and treated with

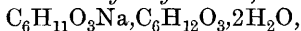


sodium hydrogen carbonate, the filtrate giving sodium  $\alpha$ -hydroxyisohexoate, long plates (from alcohol), after concentration. This salt, as well as the ammonium, potassium, sodium hydrogen, potassium hydrogen, and calcium salts, is exceedingly sweet, being about ten times sweeter than sucrose. Since all the salts and the acid in dilute solution are sweet, whilst the solid acid and its ester are not, the taste must be due to the  $\alpha$ -hydroxyisohexoic ion. Neither Cohen's dulcigann nor Oertly and Meyer's glucophore is present in the  $\alpha$ -hydroxyisohexoic acid molecule. Its use is recommended as a substitute for calcium lactate or "saccharin."

The influence of substituents on the sweetness has also been investigated. Both the anhydrides,  $C_4H_9 \cdot CH \begin{smallmatrix} CO \cdot O \\ \diagup \quad \diagdown \\ O \cdot CO \end{smallmatrix} CH \cdot C_4H_9$  and  $C_4H_9 \cdot CH(OH) \cdot CO \cdot O \cdot CH(CO_2H) \cdot C_4H_9$ , are bitter, but become sweet by boiling with alkalis. The acetyl derivative tastes like ether; its calcium salt is tasteless, but becomes sweet at  $100^\circ$ , owing to the formation of calcium  $\alpha$ -hydroxyisohexoate. Alkyl-leucic acids and their salts resemble the acetyl derivative.

The author has found that *d*-glutamic acid is twice as sweet as the *dl*-acid, and also that the sweetness of a metallic  $\alpha$ -hydroxyisohexoate becomes more pronounced the less the laevorotation of the salt. In accordance with this, *d*- $\alpha$ -hydroxyisohexoic acid, prepared from the *l*-acid by Walden's inversion, gives *d*-salts, which are sweetest of all; the *dl*-acid, which is also produced during the inversion, is sweeter than the *l*-acid.

The following substances are described. 1- $\alpha$ -Chloroisohexoyl chloride, b. p.  $59^\circ/11$  mm., is slightly laevorotatory; in benzene solution its rotation approaches zero, and then becomes dextrorotatory by further dilution. 1- $\alpha$ -Chloroisohexoic acid has b. p.  $113.5\text{--}114^\circ/10$  mm., and  $[\alpha] -19.8^\circ$  in 5% alcoholic solution; the ethyl ester has b. p.  $79\text{--}80^\circ/10$  mm. and  $[\alpha] -18.4^\circ$ , and the anilide, needles, decomposes at  $95\text{--}96^\circ$ . Sodium 1- $\alpha$ -hydroxyisohexoate has  $[\alpha] -25.3^\circ$ , the potassium salt, m. p.  $72^\circ$ , has  $[\alpha] -21.6^\circ$ , and the sodium hydrogen salt,



has  $[\alpha]^{20} -28.0^\circ$  (tungsten light).

CHEMICAL ABSTRACTS.

**Action of Heat on Oxalic Acid and Oxalates.** G. CALCAGNI (*Gazzetta*, 1920, 50, i, 245—251).—Hydrated oxalic acid melts at  $98^\circ$  and yields a mixture of carbon monoxide and dioxide, but not in equal volumes, at  $110\text{--}120^\circ$ . The anhydrous acid cannot be obtained by keeping the hydrated acid at a temperature somewhat above  $100^\circ$ , as the acid then sublimes and decomposes. Storage of the hydrated acid for several months in a vacuum desiccator over sulphuric acid yields an anhydrous compound, which begins to become pasty and to decompose at  $135^\circ$ , complete fusion and vigorous decomposition and distillation occurring at  $160^\circ$ . The melting point, given as  $186\text{--}187^\circ$  by Staub and Smith and as  $189.5^\circ$  by Althausen and Bamberger, could not be confirmed. The products yielded when various oxalates are decomposed by heat have also been investigated. [See *J. Soc. Chem. Ind.*, 1920, 501A.]

T. H. P.

**Preparation of Formaldehyde.** MOYER DELWYN THOMAS (*J. Amer. Chem. Soc.*, 1920, **42**, 867—882).—The oxidation of methyl alcohol to formaldehyde by passing a mixture of air and methyl alcohol vapour over spirals of copper, silver, and gold, respectively, at 400° has been investigated. It is shown that silver is a more active catalyst than copper or gold in the dehydrogenation of methyl alcohol, and at the same time it produces less decomposition of the formaldehyde, so that the yield of formaldehyde is very much greater with silver than with gold or copper. With silver, an absolute yield of 95% and a process yield of 55·6% were obtained when the reaction mixture contained 0·25 gram of oxygen per gram of alcohol. Under similar conditions with gold, the absolute yield was 90·5% and the process yield 50·5%, whilst the values for copper were 88·5% and 40% respectively. The best process yields were obtained with silver and gold, when the reaction mixture contained 0·4—0·5 gram of oxygen per gram of alcohol. With copper, this value was higher, 0·55—0·65 gram of oxygen per gram of alcohol. The optimum speed of the air for all three catalysts was 125—150 litres per hour. The length of the catalyst spiral did not exert a very marked influence on the process. The temperature of the reaction was measured for gold, and found to vary between 520° and 900°, according to the conditions, although the spiral was only heated to 400° to start the reaction, and then the heating was stopped. Using gold, 1·7% of acetone or 10% of water in the alcohol did not appreciably influence the process. The process consists in dehydrogenation, followed by the oxidation of hydrogen and carbon monoxide.

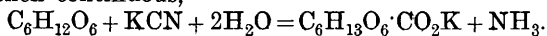
J. F. S.

**Physico-chemical Studies of Mixtures of Water, Acetaldehyde, and Paracetaldehyde.** PAUL PASCAL and DUPUY (*Bull. Soc. chim.*, 1920, [iv], **27**, 353—362).—The authors have determined the solubility of paracetaldehyde in water, and of water in paracetaldehyde over the temperature range 6—85°, and have shown that the solubility of paracetaldehyde in water is much diminished by the presence of 5% of sulphuric acid. The relative solubility of acetaldehyde in paracetaldehyde and in water increases with rise in temperature, and still further increases if sulphuric acid is present in the water.

Finally, the authors have determined the densities ( $D_4^1$  and  $D_4^{20}$ ) of paracetaldehyde and mixtures of paracetaldehyde and water, acetaldehyde and water, and acetaldehyde and paracetaldehyde in varying proportions.

W. G.

**Action of Hydrocyanic Acid on Dextrose; Kiliani's Reaction.** J. BOUGAULT and J. PERRIER (*Compt. rend.*, 1920, **170**, 1186—1189).—The combination of hydrogen cyanide with dextrose to give ammonium glucoheptonate does not take place in a feebly acid medium. A trace of alkali is sufficient to start the action, which is then continuous,



It is shown that the action of potassium cyanide on dextrose is bimolecular.

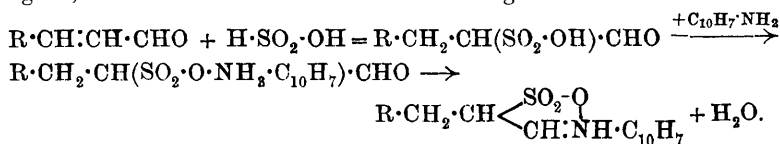
W. G.

**Purification of Celluloses. Action of Alkaline Earths on their Incrustations and on Hydro- and Oxy-celluloses.**

CARL G. SCHWALBE and ERNST BECKER (*J. pr. Chem.*, 1919, [ii], 100, 19—47).—The action of the hydroxides of calcium, strontium and barium, and of magnesium oxide on a number of hydro- and oxy-celluloses has been investigated, the actions generally being carried out at the boiling point of the solutions at the ordinary pressure. The authors are led to the following conclusions. Hydro- and oxy-celluloses are mixtures of celluloses and their degradation products. In the case of the hydrocelluloses from cotton or from wood, the latter are present in amounts of about 24—36%. Bleaching powder oxycellulose contains about 60% of pure cellulose and 40% of apparently oxidised degradation products. Sulphite celluloses contain cellulose dextrans, either naturally or formed during the process of boiling, which can be removed by boiling with lime. A variety of cellulose which is practically without reducing power is obtained by the action of boiling milk of lime on all sulphite celluloses, hydro- and oxy-celluloses. Sulphite wood celluloses lose up to 50% of their pentosan content when boiled with lime, whilst also the methyl content is depressed, sometimes to a considerable extent; the residue, however, still retains pentosans in very stable combination. Treatment with lime removes but little from soda wood celluloses, since any cellulose dextrans which may be present are dissolved during the boiling with alkali. [See, further, *J. Soc. Chem. Ind.*, 1920, July.]

H. W.

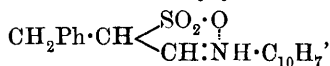
**Lignin and Reactions of Lignin.** PETER KLASON (*Ber.*, 1920, 53, [B], 706—711. Compare this vol., i, 148).—Further examination of  $\beta$ -naphthylamine lignosulphonate leads the author to ascribe to it a constitution different to that previously given, since it is now shown that only a portion of the  $\beta$ -naphthylamine is precipitated when the salt is gently warmed with dilute alkali, and that the salt is readily regenerated by the addition of  $\beta$ -naphthylamine hydrochloride to the filtered solution. The formation of the salt is considered to indicate the presence of the group  $R \cdot CH : CH \cdot CHO$  in lignin, and reaction is formulated according to the scheme



The compound is thus an internal ammonium salt in which the opening of the ring under the influence of alkali can occur in either of two directions, yielding either the alkali salt of the acid,  $R \cdot CH_2 \cdot CH \cdot (CH \cdot N \cdot C_{10}H_7) \cdot SO_3H$ , or the alkali salt of lignin-sulphonic acid and free  $\beta$ -naphthylamine. The salt is formed in

greater quantity from old than from fresh sulphite liquors, so that it would appear that the group  $R\cdot CH:CH\cdot CH_2\cdot OH$  is present in the latter, and that the aldehyde is gradually formed in them by atmospheric oxidation.

The simplest aromatic substances containing these groups are cinnamaldehyde and cinnamyl alcohol. The colorations given by the former with phloroglucinol and Wiesner's reagent closely resemble those obtained with lignin. Also, when it is treated with the sulphite acid solution at  $100^\circ$  and the "reversible" sulphite is removed, the residual solution readily yields the cyclic salt,



on treatment with  $\beta$ -naphthylamine hydrochloride, the properties of which are strikingly similar to those of  $\beta$ -naphthylamine lignin-sulphonate.

A consideration of these results and of others obtained by himself and different investigators leads the author to the conclusion that a hypothetical coniferylaldehyde (and coniferyl alcohol) are the most important and sole chemically active constituents, at any rate of coniferous lignin.

H. W.

**Some Synthetic Peptides.** (MLLE) L. PETRESCU (*Bul. Soc. Chim. România*, 1919, **1**, 56—60).—Phenylaminoacetic acid, when condensed with bromoacetyl chloride, yields *bromoacetylphenylglycine*,  $CH_2Br\cdot CO\cdot NH\cdot CHPh\cdot CO_2H$ , m. p.  $140^\circ$ , which, when treated with ammonia, gives *glycylphenylglycine*,



m. p.  $226^\circ$ , giving a copper salt and an anhydride, 3:6-diketo-2-phenylpiperazine,  $CH_2 < \begin{matrix} CO\cdot NH \\ NH\cdot CO \end{matrix} > CHPh$ , m. p.  $232^\circ$ . W. G.

**New Preparation of Amines by Catalysis.** A. MAILHE (*Compt. rend.*, 1920, **170**, 1120—1123).—When the aldazines, obtained by the condensation of aldehydes with hydrazine, are passed together with hydrogen over reduced nickel at  $140$ — $160^\circ$ , they do not yield symmetrical hydrazines, but the corresponding primary and secondary amines, the relative proportions of the two amines obtained varying with the temperature of hydrogenation and the aldazine used.

W. G.

**Catalytic Hydrogenation of Ketazines.** A. MAILHE (*Compt. rend.*, 1920, **170**, 1265—1267. Compare preceding abstract).—By hydrogenation with reduced nickel as a catalyst, the ketazines yield primary amines at low temperatures and a mixture of primary and secondary amines at higher temperatures. Thus dimethylketazine at  $130$ — $131^\circ$  yields *isopropylamine*, and, in larger amount, *diisopropylamine*. Diethylketazine, b. p.  $160$ — $163^\circ$ , yields at  $160$ — $170^\circ$  chiefly  $\gamma$ -aminopentane,  $CH_2Me\cdot CH(NH_2)\cdot CH_2Me$ , b. p.  $84^\circ$ , giving a hydrochloride and a phenylcarbamide, m. p.  $148^\circ$ . Diisopropylketazine at  $170$ — $180^\circ$  gives, as the chief product,  $\gamma$ -amino- $\beta\delta$ -

*dimethylpentane*,  $\text{CHMe}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CHMe}_2$ , b. p. 125—127°, giving a *phenylcarbamide*, m. p. 139—140°. Dipropylketazine at 170° gives  $\delta$ -*aminoheptane*,  $\text{CH}_2\text{Me} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{CH}_2\text{Me}$ , b. p. 135—136°, giving a *hydrochloride* and a *phenylcarbamide*, m. p. 134°. Diisobutylketazine at 215—220° yields  $\delta$ -*amino-}\beta\zeta*-*dimethylheptane*,  $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{CHMe}_2$ , b. p. 175—177°, together with some *di-diisobutylcarbinylamine*,  

$$[(\text{CHMe}_2 \cdot \text{CH}_2)_2 \cdot \text{CH}]_2\text{NH}.$$

W. G.

**The Acylation of Thiocarbamides.** AUGUSTUS EDWARD DIXON and JOHN TAYLOR (T., 1920, 117, 720—728).

**New Methods of Synthesis of Nitriles by Catalysis.** ALPHONSE MAILHE (*Ann. Chim.*, 1920, [ix], 13, 183—228).—A résumé of work already published (compare A., 1917, i, 686; 1918, i, 68, 105, 256, 336, 389, 532; this vol., i, 224, 377, 378, 380).

W. G.

**Electrolytic Preparation of Potassium Ferricyanide.** O. W. BROWN, C. O. HENKE, and I. L. MILLER (*J. Physical Chem.*, 1920, 24, 230—237).—The electrolytic oxidation of potassium ferrocyanide has been investigated. Using an undivided cell with electrodes of various shapes and with stirred and non-stirred solutions, the maximum yield was about 50%. When a diaphragm was used with a current density of 0.90 amp. per sq. dm., potassium hydroxide was found in both compartments of the cell, and a current efficiency of about 98% was obtained. The presence of potassium hydroxide increases the current efficiency and decreases the voltage slightly. By leaving a space in the electrolysis vessel and operating a stirrer above the gauze anode, the ferricyanide can be forced below the electrode, where it crystallises, instead of on the anode, where it would cause voltage losses. All the ferrocyanide decomposed is not converted into ferricyanide. Different current efficiencies are obtained with different electrode materials, and in all cases the maximum current efficiency is reached when the electrolysis has been in progress for about four hours. The following maximum current efficiencies were obtained, working with an anode  $7\frac{1}{2}$  cm.  $\times$   $11\frac{1}{2}$  cm. and a current of 0.95 amp.: copper 96.3%, nickel 97.7%, platinum 96.6%, Acheson graphite 99.7%, and lead covered with lead dioxide 93%.

J. F. S.

**Action of Hydrazine Hydrate on Glycerides of Higher Fatty Acids. I.** P. FALCIOLA (*Gazzetta*, 1920, 50, i, 162—165. Compare Falcicola and Mannino, A., 1915, i, 59).—The action of hydrazine hydrate on triolein, tristearin, and various other derivatives of oleic and stearic acids yields compounds which correspond perfectly in their chemical and physical properties with the hydrazides studied by Curtius (A., 1896, i, 34, and elsewhere), and rapidly reduce Fehling's solution and ammoniacal silver nitrate solution. Further, the double linking of the oleic acid residue

appears to undergo hydrogenation during the action of the hydrazine hydrate, the compounds obtained from triolein and tristearin exhibiting the same melting point, which remains unaltered when the two compounds are mixed in various proportions. The identity of the two compounds is not definitely established, but they exhibit similar cryoscopic behaviour in *p*-nitrobenzaldehyde and similar ebullioscopic behaviour in benzene; further, the hydrazide obtained from triolein does not respond to the ordinary reactions for compounds with a double linking in the molecule.

The *hydrazide*,  $C_{17}H_{35}\cdot CO\cdot NH\cdot NH_2$ , obtained from tristearin, forms white leaflets, m. p.  $115^\circ$ , and that from triolein, white leaflets, m. p.  $114.5\text{--}115^\circ$ . Similarly, ethyl oleate yields a compound, m. p.  $114\text{--}115^\circ$ , and ethyl chloro-oleate or chlorostearate a compound, m. p.  $111\text{--}114^\circ$ .

With zinc and acetic acid, the two hydrazides yield a crystalline product of lower melting point, with permanganate in acetic acid a white *compound*, m. p. (crude)  $70\text{--}76^\circ$ , and with sulphuric and nitric acids together a *compound*, m. p. (crude)  $55\text{--}60^\circ$ .

T. H. P.

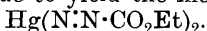
**The Production of Ethylarsinic Acid.** AMAND VALEUR and RAYMOND DELABY (*Bull. Soc. chim.*, 1920, [iv], **27**, 366—370).—The authors have repeated Dehn's work on the action of ethyl iodide on tripotassium arsenite in alcoholic solution (compare A., 1906, i, 341), and find that the action is much slower and less complete than is stated by that author. The ethyl iodide disappears much more rapidly than corresponds with the amount of arsenite converted into ethylarsinate. If the action is carried out in aqueous solution, there is not this loss of ethyl iodide, and the action is fairly complete at the end of twenty-five days.

W. G.

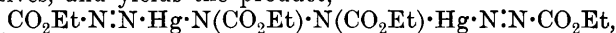
**New Mercury Compounds obtained by the Oxidation of Hydrazines by Mercuric Oxide.** OTTO DIELS and SIBYLLE UTHEMANN (*Ber.*, 1920, **53**, [B], 723—731).—When an aqueous solution of ethyl hydrazinecarboxylate is treated with yellow mercuric oxide without precautions being taken to moderate the temperature, an energetic action occurs, and large volumes of gas are evolved, consisting mainly of nitrogen, but containing also carbon monoxide and small quantities of an odoriferous substance, which is probably ethyl azidoformate; the aqueous solution contains ethyl hydrazodicarboxylate, m. p.  $130^\circ$ , and a beautifully crystalline mercury salt,  $C_{12}H_{20}O_8N_2Hg_2$ , needles, m. p.  $155^\circ$ . The formula  $CO_2Et\cdot N(Hg\cdot CO_2Et)\cdot N(Hg\cdot CO_2Et)\cdot CO_2Et$  is assigned to the latter, since it is decomposed by hydrochloric acid into mercuric chloride, ethyl hydrazodicarboxylate, carbon monoxide, and alcohol; by bromine in benzene solution into mercuric bromide, ethyl azodicarboxylate, and ethyl bromoformate, and by piperidine into mercury, ethyl hydrazodicarboxylate, and piperylurethane (ethyl piperidine-*N*-carboxylate). Methyl hydrazinecarboxylate reacts with yellow mercuric oxide in a precisely similar manner,

yielding methyl hydrazodicarboxylate and the mercury salt,  $\text{CO}_2\text{Me}\cdot\text{N}(\text{Hg}\cdot\text{CO}_2\text{Me})\cdot\text{N}(\text{Hg}\cdot\text{CO}_2\text{Me})\cdot\text{CO}_2\text{Me}$ , m. p.  $215^\circ$ .

The authors consider that their experiments lend some support to the hypothesis that di-imide or its derivatives are the primary products of the oxidation of hydrazines. In the present instance, they suppose that ethyl di-imidecarboxylate is first formed,  $\text{NH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et} + \text{HgO} = \text{H}_2\text{O} + \text{Hg} + \text{NH}\cdot\text{N}\cdot\text{CO}_2\text{Et}$ , which further reacts with mercuric oxide to yield the mercury salt,



The latter then exhibits the tendency common to many simply substituted hydrazines of passing into symmetrical disubstituted derivatives, and yields the product,



which in the manner of a diazonium compound loses nitrogen and gives the mercury salt. H. W.

**Kinetics of the Chlorination of Benzene.** F. BOURION (*Compt. rend.*, 1920, **170**, 1319—1321).—In the chlorination of industrial benzene in the presence of iron as a catalyst, the yield of monochlorobenzene increases with the velocity of chlorination. For a given time and a given concentration, the fraction of a molecule of benzene converted into monochlorobenzene is 8.5 times greater than the fraction of a molecule of chlorobenzene converted into *p*-dichlorobenzene. The yield of monochlorobenzene decreases slightly with rise in temperature. W. G.

**The Chlorination of *m*-Dichlorobenzene.** S. C. J. OLIVIER (*Rec. trav. chim.*, 1920, **39**, 411—413).—The principal product of the chlorination of *m*-dichlorobenzene in the presence of aluminium chloride is 1:2:4-trichlorobenzene. The results obtained confirm those of Cohen and Hartley (T., 1905, **87**, 1364), but refute those of Mouneyrat and Pouret (compare A., 1899, i, 263). W. G.

***o*-Chlorodinitrotoluenes.** I. GILBERT T. MORGAN and HARRY DUGALD KEITH DREW (T., 1920, **117**, 784—793).

**Preparation of certain Iodo-compounds.** CUTHBERT WILLIAM JAMES, JAMES KENNER, and WILFRID VICTOR STUBBINGS (T., 1920, **117**, 773—776).

***p*- $\beta\beta$ -Dimethylpropylbenzenesulphonic Acid and certain of its Derivatives.** ARTUR BYGDÉN (*J. pr. Chem.*, 1919, [ii], **100**, 1—18).— $\alpha$ -Phenyl- $\beta\beta$ -dimethylpropane (A., 1913, i, 29) is converted by sulphuric acid containing 6% of sulphur trioxide into *p*- $\beta\beta$ -dimethylpropylbenzenesulphonic acid,  $\text{CMe}_3\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ , the yield being about 95%; the acid forms long, colourless leaflets or large rectangular plates ( $+2\text{H}_2\text{O}$ ), which, when preserved over concentrated sulphuric acid, are transformed into the *monohydrate*, m. p.  $142.2$ — $144.2^\circ$  in an open,  $145.6$ — $146.6^\circ$  (corr.) in a closed, capillary. The constitution of the acid is deduced from its conversion into *p*-hydroxybenzoic acid by oxidation with chromic acid

in dilute sulphuric acid, and subsequent fusion of the product with sodium hydroxide, and by its oxidation by permanganate to *p*-sulphobenzoic acid. The following salts are described: *potassium*, +  $\text{H}_2\text{O}$ ; *rubidium*, +  $\text{H}_2\text{O}$ ; *caesium*, +  $\frac{1}{2}\text{H}_2\text{O}$ ; *sodium*, +  $2\text{H}_2\text{O}$ ; *lithium*, +  $\text{H}_2\text{O}$ ; *calcium*, +  $\frac{1}{2}\text{H}_2\text{O}$ ; *strontium*, +  $2\text{H}_2\text{O}$ ; *barium*, +  $3\text{H}_2\text{O}$ ; *magnesium*, +  $7\text{H}_2\text{O}$ ; *zinc*, +  $6\text{H}_2\text{O}$ ; *cadmium*, +  $3\text{H}_2\text{O}$ ; *ferrous*, +  $7\text{H}_2\text{O}$ ; *nickel*, +  $8\text{H}_2\text{O}$ ; *cobalt*, +  $8\text{H}_2\text{O}$  (?); *lead*, +  $2\text{H}_2\text{O}$ ; *copper*, +  $6\text{H}_2\text{O}$ ; *silver*, +  $1\text{H}_2\text{O}$ ; *ammonium*, anhydrous; *methylammonium*, +  $\frac{1}{2}\text{H}_2\text{O}$ , m. p. about  $225^\circ$  after much softening at about  $150^\circ$ ; *ethylammonium*, m. p.  $114$ — $115^\circ$  (corr.) after previous softening; *brucine*, m. p.  $211.0$ — $212.0^\circ$  (corr.). *p*- $\beta\beta$ -*Dimethylpropylbenzenesulphonyl chloride* forms colourless, rectangular plates or prisms, m. p.  $58.7$ — $59.2^\circ$  (corr.), whilst the corresponding *bromide*, plates, has m. p.  $65.5$ — $66^\circ$  (corr.). The sulphonyl chloride is converted in the usual manner into the *amide*, needles, m. p.  $101^\circ$  (corr.), the *methylamide*, rhombic plates, m. p.  $94.8$ — $95.3^\circ$  (corr.), the *anilide*, monoclinic plates, m. p.  $137^\circ$  (corr.), the *methylanilide*, colourless needles, m. p.  $97.8$ — $98.0^\circ$  (corr.), the *o-toluidide*, thin, shining leaflets, m. p.  $156$ — $157^\circ$  (corr.), the *p-toluidide*, rhombic plates, m. p.  $117.9$ — $118.2^\circ$  (corr.), and the *benzylamide*, six-sided plates or colourless needles, m. p.  $141.5$ — $141.7^\circ$  (corr.). *p*- $\beta\beta$ -*Dimethylpropylphenol*,  $\text{CMe}_3\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , small needles, m. p.  $118.0$ — $118.2^\circ$  (corr.), is obtained by fusing potassium *p*- $\beta\beta$ -dimethylpropylbenzenesulphonate with potassium hydroxide, and subsequent acidification of the product.

H. W.

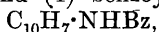
**Preparation of *p*-Phenylenediamine and Aniline from their corresponding Chlorobenzenes.** ARMAND J. QUICK (*J. Amer. Chem. Soc.*, 1920, **42**, 1033—1042).—The catalytic influence of copper salts on the reaction between ammonia and chlorobenzene (D.R.-P. 204951) or *p*-dichlorobenzene (D.R.-P. 202171) is not connected with the formation of copper ammonium compounds, since nickel, cobalt, and zinc salts, which form similar compounds, have no influence. Cuprous are more effective than cupric salts, which probably only become effective when reduced, and water cannot be replaced by alcohol as a solvent in the reaction. The reaction with dichlorobenzene is best carried out above  $200^\circ$ ; with 5—6% solutions of ammonia, the reaction is very incomplete, and an amorphous, red product is also produced. Addition of iron filings or activated charcoal to the cuprous salt improves the appearance of the final product, but with concentrated solutions of ammonia they, particularly the former, tend to retard the reaction. The action of ammonia on chlorobenzene under the conditions prescribed gave only a 39% yield, as against 80% claimed by the patent. Increase in concentration of ammonia beyond 14%, or in working temperature beyond  $200^\circ$ , does not improve the yield, although the latter is necessary for complete decomposition of the chlorobenzene. Cuprous iodide has no catalytic value for this reaction. Diphenylamine could not be



obtained from bromobenzene under the conditions prescribed by D.R.-P. 187870. J. K.

**Nitration of Aceto-*m*-toluidide.** JAMES WILFRED COOK and OSCAR LISLE BRADY (T., 1920, 117, 750—753).

**$\alpha$ -Aminophenyl- $\alpha$ -naphthylmethane.** I. SERGIO BERLINGOZZI (*Gazzetta*, 1920, 50, i, 215—221).—By reducing the two stereoisomeric oximes of phenyl  $\alpha$ -naphthyl ketone by means of zinc and hydrochloric acid, Poccianti (A., 1915, i, 822) obtained aminophenyl- $\alpha$ -naphthylmethane hydrochloride, which agrees in properties with the hydrochloride prepared by Busch and Leefhelm (A., 1908, i, 152) from magnesium  $\alpha$ -naphthyl bromide and hydrobenzamide. The latter authors give m. p. 121° for the corresponding free base, whereas the present author finds m. p. 56—59° for the base derived from Poccianti's hydrochloride. In the formation of the latter, the Beckmann transformation may possibly result in the change  $\text{OH}\cdot\text{N}:\text{CPh}\cdot\text{C}_{10}\text{H}_7 \rightarrow \text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$ , so that the base would then have the formula  $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$  instead of  $\text{C}_{10}\text{H}_7\cdot\text{CHPh}\cdot\text{NH}_2$ . That such change does not occur and that the base is actually a primary amine is shown by the facts that: (1) the same base is obtained when the oxime is reduced by means of sodium amalgam in acetic acid solution, (2) the action of nitrous acid converts the base into the corresponding alcohol, phenyl- $\alpha$ -naphthylcarbinol, (3) the base readily yields the corresponding *p*-hydroxybenzylidene derivative when treated with *p*-hydroxybenzaldehyde, and (4) benzoyl- $\alpha$ -naphthylamine.



is not reduced by sodium amalgam.

$\alpha$ -Aminophenyl- $\alpha$ -naphthylmethane,  $\text{C}_{10}\text{H}_7\cdot\text{CHPh}\cdot\text{NH}_2$ , forms rosettes of long, colourless, prismatic crystals, m. p. 56—59°, and its acetate, shining, white scales, m. p. 119°. The *p*-hydroxybenzylidene derivative,  $\text{C}_{10}\text{H}_7\cdot\text{CHPh}\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , crystallises in tufts of minute, acicular crystals, m. p. 235°. T. H. P.

**The Preparation of Picric Acid. Influence of the Degree of Sulphonation of the Phenol on the Yields of Trinitrophenol.** MAURICE M. DOLL (*Bull. Soc. chim.*, 1920, [iv], 27, 370—374).—Other things being equal, the yield of trinitrophenol increases regularly with the degree of sulphonation of the phenol.

W. G.

**Identification of Acids. V. *p*-Halogenophenacyl Esters.** W. LEE JUDEFIND and E. EMMET REID (*J. Amer. Chem. Soc.*, 1920, 42, 1043—1055).—Certain of the phenacyl esters previously described (A., 1919, i, 157) are oils or solids of low melting point. It is now shown that derivatives with a convenient range of melting points are, in general, easily obtained from *p*-halogenophenacyl bromides. The esters of aspartic, maleic, racemic, tartaric, and mucic acids derived from *p*-bromo- and *p*-chloro-phenacyl bromides decomposed without melting, whilst the salts of linoleic,

oleic, oxalic, monochloroacetic, trichloroacetic, and formic acids did not react. A liquid ester was obtained from  $\alpha$ -hydroxybutyric acid, and gallic acid gave only a small quantity of an unsatisfactory product. *p*-Iodophenacyl bromide (*o*-bromo-*p*-iodoacetophenone),  $C_6H_4I \cdot CO \cdot CH_2Br$ , yellow crystals, m. p.  $113.5^\circ$ , is obtained by brominating *p*-iodoacetophenone. *p*-Bromophenacyl alcohol,  $C_6H_4Br \cdot CO \cdot CH_2 \cdot OH$ , m. p.  $136.6^\circ$ , and *p*-iodophenacyl alcohol, m. p.  $152^\circ$ , were obtained from the acetates by the action of barium carbonate. The following esters were prepared (the temperatures indicating melting points):

*p*-Chlorophenacyl acetate,  $67.2^\circ$ ; aconitate,  $169^\circ$ ; benzoate,  $118.6^\circ$ ; ethylglycollate,  $94.4^\circ$ ; succinate,  $197.5^\circ$ ; thiocyanate,  $135.2^\circ$ ; tricarballoylate,  $125.6^\circ$ .

*p*-Bromophenacyl acetate,  $85^\circ$ ; aconitate,  $186^\circ$ ; anisate,  $152^\circ$ ; benzoate,  $119^\circ$ ; butyrate,  $63.2^\circ$ ; isobutyrate,  $76.8^\circ$ ; decoate,  $66^\circ$ ; hexoate,  $71.6^\circ$ ; octoate,  $65.5^\circ$ ; cinnamate,  $145.6^\circ$ ; citrate,  $148^\circ$ ; erucate,  $61^\circ$ ; ethylglycollate,  $104.8^\circ$ ; glycollate,  $138^\circ$ ; hippurate,  $151^\circ$ ;  $\beta$ -phenylpropionate,  $104^\circ$ ; lactate,  $112.8^\circ$ ; laevulate,  $84^\circ$ ; margarate,  $78.2^\circ$ ; palmitate,  $81.5^\circ$ ; phenylacetate,  $89^\circ$ ; propionate,  $59^\circ$ ; pyromucate,  $138.5^\circ$ ; salicylate,  $140^\circ$ ; sebacate,  $147^\circ$ ; sorbate,  $129^\circ$ ; stearate,  $78.5^\circ$ ; succinate,  $211^\circ$ ; thiocyanate,  $146.5^\circ$ ; *o*-toluate,  $56.9^\circ$ ; *m*-toluate,  $108^\circ$ ; *p*-toluate,  $153^\circ$ ; tricarballoylate,  $138.2^\circ$ ; valerate,  $63.6^\circ$ ; isovalerate,  $68^\circ$ .

*p*-Iodophenacyl acetate,  $114^\circ$ ; benzoate,  $126.5^\circ$ ; butyrate,  $81.4^\circ$ ; isobutyrate,  $109.2^\circ$ ; decoate,  $80^\circ$ ; hexoate,  $81.5^\circ$ ; octoate,  $77^\circ$ ; isovalerate,  $78.8^\circ$ ; erucate,  $73.8^\circ$ ; lactate,  $139.8^\circ$ ; margarate,  $88.8^\circ$ ; palmitate,  $90^\circ$ ; propionate,  $94.9^\circ$ ; stearate,  $90.5^\circ$ ; valerate,  $78.6^\circ$ .

J. K.

**Polymerisation in Ethereal Solution by means of Ferric Chloride. Seventh Polymeride of Anethole.** E. PUXEDDU (*Gazzetta*, 1920, **50**, i, 149—154. Compare A., 1913, i, 460; 1916, i, 806).—Addition of ethereal ferric chloride solution to an ethereal solution of anethole results in the immediate precipitation of a white substance; fractional distillation of the latter under reduced pressure yielding a new polymeride, the seventh known, of anethole. The author and Marica (A., 1916, i, 807) consider that eleven such isomeric polymerides are possible, although Orndorff and Morton (A., 1900, i, 289) maintain that phenols containing a propenylic chain are able to exist in only two isomeric forms. The author has prepared in the pure state the *p*-butenyl- and *p*-isopentenyl-anisoles described by Moureu and Chauvet (A., 1897, i, 403), and has studied their bromides and polymerides.

The seventh polymeride of anethole,  $(C_{10}H_{12}O)_n$ , forms prismatic crystals, m. p.  $132^\circ$ ; owing to lack of material, its molecular weight was not determined.

*p*-Butenylanisole has b. p.  $245$ — $248^\circ$ , and yields a dibromide, which was not analysed, and, when treated with ethereal ferric chloride, a dense, oily polymeride.

*p*-isoPentenylanisole forms a colourless, faintly opalescent liquid,

b. p. 248—252°,  $n$  1.54, with the odour of aniseed. The bromide (not analysed) forms long, slender needles, m. p. 93—95°, and the polymeride a dense, gummy mass. T. H. P.

***o*-Anisyltellurium Compounds.** KARL LEDERER (*Ber.*, 1920, **53**, [B], 712—716. Compare A., 1917, i, 134; this vol., i, 40).—Di-*o*-anisyl telluride has been prepared by the action of magnesium *o*-anisyl bromide on tellurium dibromide; it is purified by conversion into the crystalline dibromide, and reduction of the latter with magnesium methyl iodide.

*Di-o-anisyl telluride*,  $\text{Te}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$ , is a colourless, crystalline substance, m. p. 73—74°, b. p. 248—251°/30 mm., which gives rise to the following *di-o-anisyltelluronium* compounds in the usual way: *dichloride*, microscopic rods, m. p. 184—185° after softening at 182°; *dibromide*, small, monoclinic platelets, m. p. 195—196° after softening at 192°; *di-iodide*, shining, metallic, iodine-coloured needles, m. p. 199—200° after softening at 198°; *oxide*,

$\text{TeO}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$ , needles, m. p. 205—206°; *methiodide*, small rods, m. p. 124—125°. It also forms *additive* compounds with mercuric haloids, as follows: *iodide*,  $\text{Te}(\text{C}_6\text{H}_4\cdot\text{OMe})_2\cdot\text{HgI}_2$ , yellow crystals, m. p. 80—81° after softening at 79°; *bromide*, yellow crystals, m. p. about 84° after softening at 70°; *chloride*, obtained as an oil, which, after solidification, has m. p. 143—144°, and after recrystallisation has m. p. 156—157° (decomp.) after softening at 150°. H. W.

**Relationship between Chemical Constitution and Physiological Action in Local Anæsthetics. I. Homologues of Procaine.** OLIVER KAMM (*J. Amer. Chem. Soc.*, 1920, **42**, 1030—1033).— $\gamma$ -Diethylaminopropyl *p*-nitrobenzoate hydrochloride, from *p*-nitrobenzoyl chloride and  $\gamma$ -diethylaminopropyl alcohol, m. p. 189—190°, on reduction with tin and hydrochloric acid gives  $\gamma$ -diethylaminopropyl *p*-aminobenzoate, m. p. 69° (*hydrochloride*, needles, m. p. 164°), which is structurally similar to cocaine, and in physiological action is intermediate between this drug and procaine (novocaine). It is slightly more toxic, but considerably more effective as a surface anæsthetic than the latter.  $\gamma$ -Diethylaminopropyl *m*-nitrobenzoate hydrochloride, m. p. 139—140°, yields  $\gamma$ -diethylaminopropyl *m*-aminobenzoate, a colourless oil, which solidifies only at a low temperature (*hydrochloride*, m. p. 151°).

J. K.

**The Constitution of Acylanthranils.** GUSTAV HELLER (*Ber.*, 1920, **53**, [B], 731—732).—A further contribution to the discussion on this subject (compare Heller and Lauth, this vol., i, 181; Schröter, this vol., i, 333). The author maintains his original views, and points out that the properties of the crystalline additive products of hydrazine and lactones differ considerably from those of the substances formed from hydrazine and acylanthranils, particularly from the point of relative stability. H. W.

**$\beta$ -Halogenoethylaminobenzoic Esters.** J. ALTWEGG and J. LANDRIVON (U.S. Pat. 1334641).—*Ethyl p- $\beta$ -chloroethylaminobenzoate*,  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ , crystals, m. p.  $69^\circ$ , b. p.  $183^\circ/3$  mm., is obtained by adding a solution of the corresponding hydroxy-compound (20 parts) in dry benzene (15 parts) to a mixture of phosphorus pentachloride (20 parts) and dry benzene (25 parts), heating the mixture on the water-bath, evaporating the benzene and phosphoryl chloride, and distilling the residue under reduced pressure. Dimethylaniline and thionyl chloride may be used instead of benzene and phosphorus pentachloride; in this case, the product of the reaction is treated with warm water, whereby dimethylaniline hydrochloride dissolves and the ester separates in granules. Other esters may be prepared similarly. They are useful as local anaesthetics. CHEMICAL ABSTRACTS.

**$\beta$ -Alkylaminoethylaminobenzoic Alkyl Esters.** J. ALTWEGG and J. LANDRIVON (U.S. Pat. 1334642).—*Ethyl p- $\beta$ -diethylaminomethylaminobenzoate*,  $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ , an oil (hydrochloride, white needles, m. p.  $156^\circ$ ), is obtained by heating a mixture of diethylamine (2 mols.) and ethyl *p- $\beta$ -chloroethylaminobenzoate* (1 mol.) in a closed vessel for several hours at  $100^\circ$ , and treating the cooled, crystalline mass with water to dissolve diethylamine hydrochloride. The corresponding *butyl* ester has b. p.  $213\text{--}214^\circ/6$  mm., and forms a *hydrochloride*, m. p.  $127^\circ$ . *Butyl p- $\beta$ -methylaminoethylaminobenzoate*, b. p.  $214^\circ/6$  mm., forms a hydrochloride, m. p.  $141^\circ$ . CHEMICAL ABSTRACTS.

**Mechanism of the Reaction between Ketens and the Grignard Reagent.** HENRY GILMAN and L. C. HECKERT (*J. Amer. Chem. Soc.*, 1920, **42**, 1010—1014).—Hitherto, all the reactions of the ketens have been attributed to initial addition to the ethylenic linking, but, on the other hand, no case is known in which the Grignard reagent combines directly with such linkings. By direct benzoylation of the initial product of the reaction between diphenyl keten and magnesium phenyl bromide, triphenylvinyl benzoate,  $\text{CPh}_2\cdot\text{CPh}\cdot\text{O}\cdot\text{COPh}$ , was obtained, showing that addition of the Grignard reagent had taken place at the carbonyl group. J. K.

**Iodination of the Phenoxyacetic Acids.** EFISIO MAMELI, EVARISTO GAMBETTA, and GUIDO RIMINI (*Gazzetta*, 1920, **50**, i, 166—186).—Of the various methods tried for the iodination of phenoxyacetic acid and some of its substituted derivatives, the action of iodine in presence of iodic acid in chloroform solution is found to give the best results. The acids employed gave the following melting points, some of which differ slightly from those found in the literature: phenoxyacetic acid,  $99\text{--}100^\circ$ ; 2-methoxyphenoxyacetic acid,  $123\text{--}125^\circ$ ; 3-methyl-6-isopropylphenoxyacetic acid,  $147\text{--}148^\circ$ ;  $\alpha$ -naphthoxyacetic acid,  $190^\circ$ ;  $\beta$ -naphthoxyacetic acid,  $156^\circ$ .

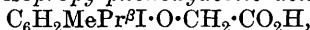
*p*-Iodophenoxyacetic acid,  $\text{C}_6\text{H}_4\text{I}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , obtained by

iodinating phenoxyacetic acid, and also by the action of chloroacetic acid on *p*-iodophenol, crystallises in shining, colourless, odourless scales, m. p. 155—156°; at first it appears tasteless, but a persistent, sweet taste gradually develops. On nitration, it yields 4-iodo-3-nitrophenol. The *potassium*, *calcium* (+ 2H<sub>2</sub>O), *silver*, and *copper* (+ 2H<sub>2</sub>O) salts were prepared and analysed. The *ethyl* ester, C<sub>10</sub>H<sub>11</sub>O<sub>3</sub>I, forms colourless, tasteless, rhombohedral plates, m. p. 62—63°, with a pronounced fruity odour. The *amide*, C<sub>8</sub>H<sub>5</sub>O<sub>2</sub>NI, crystallises in silky, white needles, m. p. 165—166°.

5-Iodo-2-methoxyphenoxyacetic acid, OMe·C<sub>6</sub>H<sub>3</sub>I·O·CH<sub>2</sub>·CO<sub>2</sub>H, prepared by iodinating 2-methoxyphenoxyacetic acid, and also by the action of chloroacetic acid on 5-iodo-2-methoxyphenol, forms slender, white, odourless, tasteless needles, m. p. 155°. By cold concentrated sulphuric acid it is coloured first violet and then brown, and afterwards charred; the sulphuric acid solution colours chloroform violet, and emits iodine vapour when heated. Similar behaviour is shown by the yellowish-brown solution obtained with concentrated nitric acid. The *potassium* and *silver* salts were prepared and analysed.

4-Iodo-2-methoxyphenoxyacetic acid, obtained from 4-iodo-2-methoxyphenol and chloroacetic acid, crystallises in white, nacreous scales, m. p. 83—84°.

4-Iodo-3-methyl-6-isopropylphenoxyacetic acid,



prepared by iodination of 3-methyl-6-isopropylphenoxyacetic acid in *isoamyl* alcohol, and also by the action of chloroacetic acid on 4-iodo-3-methyl-6-isopropylphenol, crystallises in small, white, colourless, tasteless needles, m. p. 126—127°, and towards sulphuric and nitric acids behaves similarly to 5-iodo-2-methoxyphenoxyacetic acid. Its *potassium* and *silver* salts were prepared and analysed.

1-Iodo- $\beta$ -naphthoxyacetic acid, C<sub>10</sub>H<sub>6</sub>I·O·CH<sub>2</sub>·CO<sub>2</sub>H, prepared by iodination of  $\beta$ -naphthoxyacetic acid, and also by the interaction of chloroacetic acid and 1-iodo- $\beta$ -naphthol, forms thin, white, odourless plates, m. p. 170—171°. It becomes pale yellow at 138° and pink at 145°, the colour deepening as the melting point is approached; at 203—210° it decomposes, with emission of violet vapour. Concentrated sulphuric acid decomposes it, with evolution of violet vapour, the acid assuming a brown colour with green reflexion. In cold concentrated nitric acid it is insoluble, but the hot acid dissolves it, giving a ruby-red liquid and violet vapours. The *potassium* and *silver* salts were prepared and analysed.

Iodo- $\alpha$ -naphthoxyacetic acid, C<sub>10</sub>H<sub>6</sub>I·O·CH<sub>2</sub>·CO<sub>2</sub>H, prepared by iodination of  $\alpha$ -naphthoxyacetic acid, forms slender, pink, odourless crystals, m. p. 168—170°, and decomposes, with evolution of iodine vapour, at 195°. It colours concentrated sulphuric acid violet-pink, and liberates iodine when treated with boiling concentrated nitric acid. No suitable iodo-derivative of  $\alpha$ -naphthol being known, the position of the iodine in this acid could not be established. The *potassium* and *silver* salts were prepared and analysed.

T. H. P.

**The Behaviour of Optically Active Esters on Hydrolysis.**  
ALEX. MCKENZIE and HENRY WREN (T., 1920, 117, 680—690).

**Case of Isomerism in the Series of Aromatic  $\alpha$ -Ketonic Acids.** H. GAULT and R. WEICK (*Compt. rend.*, 1920, 170, 1392—1395).—Ethyl phenylpyruvate as prepared by Bougault (compare A., 1914, i, 839) and by Hemmerlé (compare A., 1915, i, 78) is a solid, m. p.  $45^{\circ}$  (the present authors find m. p.  $51$ — $52^{\circ}$ ). By the hydrolysis of ethyl cyanophenylpyruvate in alcoholic medium, and fractional distillation of the crude product, an isomeric ethyl phenylpyruvate is obtained as a liquid, b. p.  $149^{\circ}/15$  mm., which will not solidify. This liquid isomeride gives a bisulphite compound, a semicarbazone, and a phenylhydrazone identical with those from the solid isomeride. It is shown that the solid isomeride is the unstable form, and that by slow distillation under reduced pressure it is converted into the stable liquid form, but the change is not reversible. The new method of preparation really gives a crude mixture of the two isomerides, which, during the fractional distillation, is entirely converted into the liquid form.

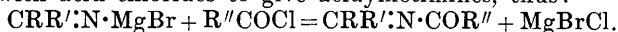
$\beta$ -Hydroxy- $\alpha$ -phenylmaleimide was isolated as an intermediate product of the hydrolysis of ethyl cyanophenylpyruvate. W. G.

**Synthesis of Bibasic Acids by the Action of Malonic Acid on Hydrols. Replacement of the Hydroxy-group by the Group  $\cdot\text{CH}(\text{CO}_2\text{H})_2$ .** R. FOSSE (*Ann. Chim.*, 1920, [ix], 13, 154—183. Compare this vol., i, 390—396).—A more detailed account of work already published (compare A., 1906, i, 975; 1907, i, 414). W. G.

**The Constitution of Some Dialkylcyclohexanones.** R. CORNUBERT (*Compt. rend.*, 1920, 170, 1259—1262. Compare A., 1914, i, 969).—A further study of the allyl derivatives obtained by the action of allyl iodide on cyclohexanone and the three methylcyclohexanones in the presence of sodamide by means of the action of benzaldehyde (compare this vol., i, 390). The constitutions of these compounds are 1-methyl-1-allylcyclohexan-2-one, giving a *benzylidene* derivative, b. p.  $211$ — $212^{\circ}/15$  mm. (corr.); 1:1-diallylcyclohexan-2-one, giving a *benzylidene* derivative, b. p.  $231$ — $232^{\circ}/18$  mm. (corr.); 1-methyl-3:3-diallylcyclohexan-4-one with a *benzylidene* derivative, m. p.  $71$ — $71.5^{\circ}$ ; and 1-methyl-2:2(or 4:4)-diallylcyclohexane-3(or 5)-one with a *benzylidene* derivative, m. p.  $45$ — $48^{\circ}$ . Similarly, other di- and tri-alkylcyclohexanones previously described (compare A., 1914; i, 951, 969) have the constitution 1-methyl-1-*n*-propylcyclohexan-2-one and 1-methyl-1:3-diallylcyclohexan-2-one. W. G.

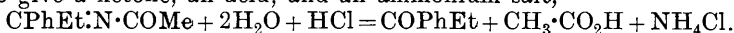
**Acidylketimines.** CHARLES MOUREU and GEORGES MIGNONAC (*Compt. rend.*, 1920, 170, 1353—1356).—Organo-magnesium

derivatives of the type  $\text{CRR}'\text{:N}\cdot\text{MgBr}$ , obtained by the condensation of nitriles,  $\text{RCN}$ , with magnesium alkyl bromides,  $\text{R}'\text{MgBr}$ , react with acid chlorides to give acylylketimines, thus:



In this way, the authors have prepared *acetylphenylethylketimine*,  $\text{CPhEt}\text{:N}\cdot\text{COMe}$ , m. p.  $126^\circ$ ; *butyrylphenylethylketimine*, m. p.  $85\cdot5^\circ$ ; *isovalerylphenylethylketimine*, m. p.  $117^\circ$ ; *benzoylphenylethylketimine*, m. p.  $165^\circ$ ; *acetylphenylisobutylketimine*, m. p.  $134^\circ$ ; and *benzoylphenylisobutylketimine*, m. p.  $160^\circ$ .

All these acylylketimines are hydrolysed by dilute mineral acids to give a ketone, an acid, and an ammonium salt,



When hydrolysed by alkalis, they give the ketone, the alkali salt of the organic acid, and ammonia.

W. G.

**The Stereoisomeric Forms of Benzoylphenylacetylene Diiodide.** CHARLES DUFRAISSE (*Compt. rend.*, 1920, **170**, 1262—1264. Compare A., 1914, i, 845).—Nef (compare A., 1900, i, 20) obtained only one di-iodide by the action of iodine on benzoylphenylacetylene. By suitably modifying Nef's process, the author has obtained two stereoisomeric di-iodides. The substance A, m. p.  $155\text{--}156^\circ$ , is the one described by Nef. The *di-iodide*, B, occurs in two distinct crystalline forms,  $B_\alpha$  and  $B_\beta$ .  $B_\alpha$  is converted into  $B_\beta$  when heated at its m. p.,  $82^\circ$ ;  $B_\beta$  has m. p.  $84\text{--}85^\circ$ , and is converted into  $B_\alpha$  by rapid cooling or rapid evaporation of its alcoholic solution.

W. G.

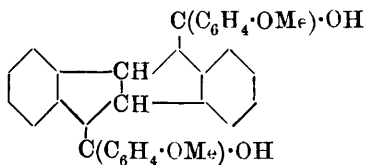
**The Diphen succindene Series. II. 2:2'-Dibenzoylbenzil and its Derivatives.** K. BRAND and H. LUDWIG (*Ber.*, 1920, **53**, [B], 809—814).—The constitution assigned previously to the brown hydrocarbon, 9:12-diphenyldiphen succindadiene (A., 1912, i, 960), is confirmed by the observation that it is oxidised by chromic acid in hot glacial acetic acid solution, with the production of two molecules of *o*-benzoylbenzoic acid from each molecule of the hydrocarbon. If, however, the oxidation is carried out in cold solution, 2:2'-*di-benzoylbenzil*,  $\text{C}_6\text{H}_4\text{Bz}\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Bz}$ , yellow crystals, m. p.  $188^\circ$ , is obtained. The latter slowly condenses with *o*-phenylenediamine in boiling glacial acetic acid solution to yield 2:3-*di(o-benzoylphenyl)-quinoxaline* (annexed formula), colourless, silky crystals, m. p.  $237\text{--}238^\circ$ . 2:2'-*Di-p-toluoylbenzil*, yellow crystals, m. p.  $191^\circ$ , is similarly formed from 9:12-di-*p*-tolyl diphen succindadiene.

H. W.

**The Diphen succindene Series. III. Coloured Phenol Ethers of the Diphen succindene Series.** K. BRAND and F. W. HOFFMANN (*Ber.*, 1920, **53**, [B], 815—821. Compare A., 1912, i, 960, and preceding abstract).—The action of magnesium *o*- and *p*-anisyl bromides on diphen succindan-9:12-dione has been investigated, and a series of derivatives have been prepared which

are closely similar to the phenyl and *p*-tolyl compounds described previously.

8 : 12-*Dihydroxy*-8 : 12-*di-o-anisyl*diphensuccindane (annexed formula) forms colourless, transparent needles, m. p. 207·5°, and

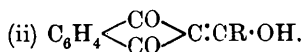


is converted by a boiling mixture of glacial acetic and formic acids into 9 : 12-*di-o-anisyl*diphensuccindadiene, reddish-brown needles, m. p. 247°. The latter is oxidised by a warm solution of

chromic acid in glacial acetic acid to 2 : 2'-*di-o-anisoylbenzil*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , pale yellow needles, m. p. 244°, which condenses with *o*-phenylenediamine to yield 2 : 3-*di*[*o-anisoylphenyl*]-*quinoxaline*, almost colourless needles, m. p. 250°.

9 : 12-*Dihydroxy*-9 : 12-*di-p-anisyl*diphensuccindane, colourless, transparent needles, m. p. 230°, is readily dehydrated to 9 : 12-*di-p-anisyl*diphensuccindadiene, brown needles, m. p. 242°. (When the Grignard reagent is prepared from *p*-anisyl iodide, the diene is sometimes the only isolable substance.) It is converted by gentle oxidation with chromic acid in glacial acetic acid into *di-p-anisoylbenzil*, yellow needles, m. p. 214°, whilst more drastic oxidation converts it into 2-*p-anisoylbenzoic* acid, m. p. 138° (the literature records m. p. 142—143°). The benzil condenses with *o*-phenylenediamine to yield 2 : 3-*di*(*p-anisoylphenyl*)-*quinoxaline*, almost colourless needles, m. p. 251°. H. W.

**Constitution of Enols. IV. Enolisation of 2-Monoacylindane-1 : 3-diones.** JOHANNES SCHEIBER and GEORG HOPFER (*Ber.*, 1920, **53**, [B], 697—706).—The enolisation of monoacylindanediones may occur in such a manner as to yield products of the formula (i)  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{OH}) \\ \text{CO} \end{smallmatrix} \text{C} \cdot \text{OR}$  or



The authors have therefore investigated the behaviour of ethyl 1 : 3-diketohydrindene-2-carboxylate, 2-acetyl- and 2-benzoyl-1 : 3-diketohydrindenones towards ozone, and in each case find that enolisation occurs, at any rate to some extent, so as to give rise to substances of the second formula.

The main products of the action of ozone on a solution of ethyl 1 : 3-diketohydrindene-2-carboxylate in carbon tetrachloride at -20° are phthalic acid and ethyl glyoxalate, which can only be derived from an enol of type (i); at the same time, considerable quantities of carbon dioxide are formed, the bulk of which is attributable to the decomposition of ethyl hydrogen carbonate, whilst smaller quantities arise from the oxidation of triketohydrindene to phthalic acid, thus indicating that enolisation also occurs in such a manner as to yield type (ii). Ozonisation of 1 : 3-diketo-

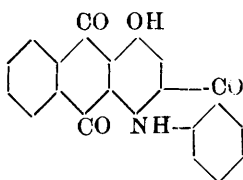


2-acetylhydrindene must produce either phthalic acid and methyl glyoxal or triketohydrindene and acetic acid, according as enolisation gives rise to type (i) or (ii); actually, the latter substances are produced, and although the absence of enolisation to type (i) is not definitely excluded, it appears certain that at least 95% of the transformed substance belongs to type (ii). It is, however, remarkable that about 60% of the original material remains unaffected by ozone, although titration by Meyer's method indicates the presence of more than 90% of enol. The products obtained from 1:3-diketo-2-benzoylhydrindene are phthalic acid, a strongly reducing substance, which is probably phenylglyoxal, benzoic acid, and carbon dioxide; triketohydrindene cannot be detected, and is probably destroyed by oxidation. Only about 80% of the original substance enters into action, although the Meyer titration method indicates an almost exclusively enolic form. It appears that about 40% of the enolised portion belongs to type (ii). H. W.

**Some Properties of Benzanthrone.** ARTHUR GEORGE PERKIN (T., 1920, 117, 696—708).

**4-Chloro-1-hydroxyanthraquinone.** FRITZ ULLMANN and ACHILLE CONZETTI (*Ber.*, 1920, 53, [B], 826—837).—1-Hydroxyanthraquinone is conveniently prepared by the diazotisation of a solution of 1-aminoanthraquinone in concentrated sulphuric acid, and is transformed by sulphuryl chloride in the presence of nitrobenzene at 100° into 4-chloro-1-hydroxyanthraquinone, which, when obtained in this manner, can only be freed with difficulty from small amounts of dichlorohydroxyanthraquinone; if the chlorination is effected in the presence of a little iodine, 2:4-dichloro-1-hydroxyanthraquinone, shining, yellow needles, m. p. 242°, is obtained. The constitution of the substances is deduced from their synthesis in the following manner: (i) phthalic anhydride is condensed with *p*-chlorophenol in acetylene tetrachloride solution in the presence of aluminium chloride to 5-chloro-2-hydroxy-*o*-benzoylbenzoic acid,  $\text{HO}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , colourless leaflets, m. p. 202° after softening slightly at 196°, which is transformed by sulphuric acid monohydrate into 4-chloro-1-hydroxyanthraquinone, small, yellow crystals, m. p. 193° (corr.); (ii) a molten mixture of phthalic anhydride and 2:4-dichlorophenol is converted by aluminium chloride into 3:5-dichloro-2-hydroxy-*o*-benzoylbenzoic acid, colourless leaflets, m. p. 204° (corr.), which is then transformed into 2:4-dichloro-1-hydroxyanthraquinone, m. p. 242°, in the usual manner. 4-Chloro-1-hydroxyanthraquinone is readily converted into 1:4-dichloroanthraquinone, m. p. 187°, by phosphorus pentachloride at 155—160° if care is taken to remove the phosphoryl chloride as rapidly as it is formed; under similar conditions, 2:4-dichloro-1-hydroxyanthraquinone gives 1:2:4-trichloroanthraquinone, m. p. 185.5° (corr.). The  $\alpha$ -chloro-atoms of the hydroxyanthraquinones may be replaced by the hydroxyl group by treatment with boric and sulphuric acids at 156—160°, thereby yielding

1:4-dihydroxyanthraquinone, m. p.  $198^{\circ}$  (corr.), and 2-chloro-1:4-dihydroxyanthraquinone, dark red, shining needles, m. p.  $239^{\circ}$ , respectively. 4-Chloro-1-hydroxyanthraquinone is transformed by *p*-toluenesulphonamide in amyl-alcoholic solution in the presence of copper and potassium acetates into 1-hydroxy-4-*p*-toluenesulphonamidoanthraquinone, orange-yellow needles, m. p.  $197^{\circ}$ , which is hydrolysed by concentrated sulphuric acid to 4-amino-1-hydroxyanthraquinone, dark red, metallic needles, m. p.  $215^{\circ}$  (Wacker, A., 1903, i, 132, gives  $207-208^{\circ}$ ). 2-Chloro-1-hydroxy-4-*p*-toluenesulphonamidoanthraquinone, pale red needles, m. p.  $198^{\circ}$ , and 2-chloro-4-amino-1-hydroxyanthraquinone, wine-red needles, m. p.  $236^{\circ}$ , are similarly derived from 2:4-dichloro-1-hydroxyanthraquinone. 1-Hydroxy-4-anilinoanthraquinone, dark violet, shining leaflets, m. p.  $161^{\circ}$ , is obtained from the monochloroanthraquinone, aniline, potassium acetate, and a trace of copper acetate. The similarly prepared 2-chloro-1-hydroxy-4-anilinoanthraquinone crystallises in dark violet needles, m. p.  $195^{\circ}$ . N[1-Hydroxyanthraquinonyl-4]-anthranilic acid is most conveniently prepared by boiling a solution of 4-chloro-1-hydroxyanthraquinone and anthranilic acid in amyl alcohol with anhydrous potassium acetate

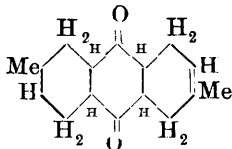


in the presence of copper acetate and copper powder; it forms bluish-violet, shining needles, m. p.  $272^{\circ}$  (corr.; decomp.). The substance is not transformed into 4-hydroxyanthraquinone-2:1-acridone (annexed formula) by sulphuric acid or phosphoric oxide, but the conversion may be effected by the action of acetic anhydride in the presence of pyridine, and subsequent treatment of the acetyl derivative so formed with *p*-toluenesulphonyl chloride; the acridone crystallises in shining, blue leaflets, m. p.  $321^{\circ}$ , and gives blue shades on cotton from a wine-red vat.

H. W.

### Condensations at Double Bonds. I. Condensation of Isoprene with *p*-Benzoquinone.

H. von EULER and K. O. JOSEPHSON (*Ber.*, 1920, **53**, [B], 822—826).—When isoprene is heated with one-sixth to one-seventh of its weight of *p*-benzoquinone for five to six hours at temperatures ranging from  $120^{\circ}$  to  $180^{\circ}$ , it readily yields a product, m. p.  $234^{\circ}$ , to which the annexed formula is assigned (in which the 2:7-position of the two methyl groups is uncertain). The mechanism of the reaction is therefore closely analogous to that of the condensation of isoprene to dimethylcyclooctadiene. The substance readily unites with bromine in glacial acetic acid



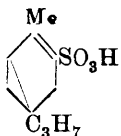
solution, yielding the tetrabromide,  $C_{16}H_{20}O_2Br_4$ , m. p.  $210^{\circ}$  (corr.; decomp.). With hydroxylamine, it gives a dioxime, which commences to decompose above  $200^{\circ}$ , and probably also a monoxime. Preliminary experiments show that it is readily oxidised by per-

manganate, and thereby undergoes very extensive decomposition. Reduction by hydrogen in ethereal solution in the presence of platinum-black appears to lead to the formation of a substance,  $C_{16}H_{26}O_2$ . H. W.

**The Camphane Series. XXXVIII. The Cyanohydrazone of Camphorquinone.** MARTIN ONSLOW FORSTER and WILLIAM BRISTOW SAVILLE (T., 1920, 117, 753—761).

**Pulegonesulphonic Acid. The Behaviour of Sabinol and Sabinene towards Sulphurous Acid and Thujone.** OTTO WALLACH [with G. REGGELIN, F. RIESENER, and HEUBNER] (*Nachr. Ges. Wiss. Göttingen*, 1919, 321—336; from *Chem. Zentr.*, 1920, i, 671—672).—Pulegonesulphonic acid is obtained as an almost colourless syrup when an alcoholic solution of pulegone is saturated with sulphur dioxide and preserved in a closed vessel for several days at  $20^\circ$ ; it forms well-crystallised salts, which obstinately retain water (the *magnesium*, *zinc*, *lead*, *barium*, *calcium*, *ammonium*, and *piperidine* compounds are described). Such of them as do not contain poisonous metals are devoid of physiological activity.

Purified sabinol is similarly converted into its *sulphonic acid* at  $0^\circ$ . (In addition, small quantities of an insoluble, amorphous substance, m. p.  $213\text{--}215^\circ$ , which appears to be an ester, and of a neutral compound, woolly needles, m. p.  $147\text{--}148^\circ$ , are obtained.) The acid has m. p.  $98\text{--}99^\circ$ , becomes discoloured, and finally liquefies on exposure to air; it behaves like an unsaturated substance towards bromine or potassium permanganate. Its constitution has not been definitely elucidated, but its conversion by potassium hydroxide solution (1:1) into an alcohol, which, after reduction and oxidation, yields thujone, b. p.  $199\text{--}200^\circ$ , indicates the annexed formula. On the other hand, an acid of this constitution should yield  $\alpha$ -thujoketonic acid when cautiously oxidised by potassium permanganate, but this product has not been obtained so far.



Sabinol is converted by hydrogenation in the presence of palladium chloride into a hydrocarbon, b. p.  $161\text{--}163^\circ$ ,  $D^{21}_D 0.795$ ,  $n_D 1.4375$ , and an alcohol, b. p.  $206\text{--}208^\circ$ ,  $D^{20}_D 0.9090$ ,  $n_D 1.4576$ , the latter being the main product. It is oxidised by the calculated quantity of chromic acid in glacial acetic acid solution to *l*-thujone, b. p.  $203\text{--}205^\circ$ ,  $D^{20}_D 0.907$ ,  $n_D 1.4507$ ,  $[\alpha]_D -30.62^\circ$  in 16.1% methyl-alcoholic solution. Potassium permanganate converts it into  $\alpha$ -thujoketonic acid. The unusually high specific rotation indicates the possible presence of a third isomeride of thujone.

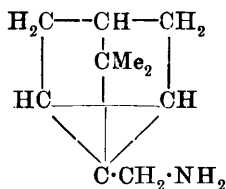
Oils containing thujone become strongly acidic when preserved, mainly owing to the formation of  $\alpha$ -thujoketonic acid. H. W.

**Homocamphor.** ARTHUR LAPWORTH and FRANK ALBERT ROYLE (T., 1920, 117, 743—750).

**Preparation and Properties of *iso*Amylcamphor and Some of its Derivatives.** FÉLIX MARTIN (*J. Pharm. Chim.*, 1920, [vii], 21, 417—425).—A mixture of *iso*amylcamphor and *iso*amylcamphol is obtained by dissolving one atomic equivalent of sodium in an excess of *iso*amyl alcohol, adding one molecular equivalent of camphor, and heating the mixture at 140° for fifteen hours under a reflux apparatus. The mixture of the two substances when oxidised with permanganate in benzene solution yields *iso*amylcamphor, a yellow, odourless oil, b. p. 165°/33 mm.,  $D_4^{25}$  0.9272,  $[\alpha]_D^{25} + 59^\circ$  (in alcohol),  $+ 38.4^\circ$  (in benzene). Reduction with sodium in alcoholic solution converts the mixture into *iso*amylcamphol, m. p. 25—28°, b. p. 190°/61 mm.,  $D_4^{25}$  0.9611,  $[\alpha]_D^{25} + 17^\circ$  (in alcohol). *iso*Amylcamphyl acetate, a colourless liquid, b. p. 169°/30 mm.,  $D_4^{25}$  0.9402,  $[\alpha]_D^{25} + 7.24^\circ$  (in alcohol), is obtained by acetylating *iso*amylcamphol. W. P. S.

**Tricyclene.** P. LIPP (*Ber.*, 1920, 53, [B], 769—781).—It has been suggested by Semmler that tricyclene is an intermediate product in the conversion of borneol or *isoborneol* into camphene. Since, however, the formulation of this substance has been doubted by Meerwein (*A.*, 1914, i, 850), although the objections he raises have been partly removed by Ruziska (*A.*, 1918, i, 398), the author has endeavoured to prepare the hydrocarbon from a similarly constituted substance, and for this purpose has chosen tricyclenic [dehydrocamphenylic] acid, the formula of which has been established with practical certainty by Komppa and Hintikka (*A.*, 1908, i, 852), and by Komppa (*A.*, 1911, i, 642). He has thereby succeeded in establishing definitely the constitution of the hydrocarbon and in showing that it is readily converted by sodium hydrogen sulphate at 160° into camphene, but not by zinc chloride in benzene solution. Tricyclene may therefore be an intermediate product in the formation of camphene from borneol, but not from *isoborneol*.

An ethereal solution of tricyclenyl chloride is converted by gaseous ammonia into tricyclenamide, shining, rhombic leaflets, m. p. 117—118° (corr.) (Komppa and Hintikka, *loc. cit.*, give 114.5°), which is transformed by phosphorus trichloride into *tricyclenylonitrile*, b. p. 100—102° (corr.)/12 mm., m. p. 65—70°. The latter is reduced by sodium and alcohol to *ω*-amino-tricyclene (annexed formula), colourless, paraffin-like mass, which melts with the warmth of the hand and has b. p. ca. 100—101°/27 mm. (the *hydrochloride*, colourless leaflets, which does not melt below 266°, and the *carbonate*, slender needles, m. p. 97—100° [slight decomp.], are described). Attempts to convert the base into the corresponding primary alcohol by means of sodium nitrite and hydrochloric acid were unsuccessful, an oily, heterogeneous product being obtained, which owed its formation to rupture of the ring system. The ease with which this occurs is

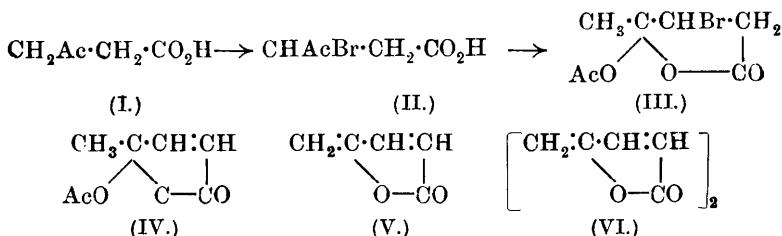


further illustrated by the conversion of  $\omega$ -aminotricyclene hydrochloride into camphenilanaldehyde and ammonia by warming for a short time with fuming hydrochloric acid.

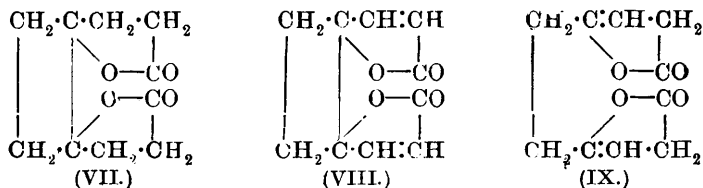
A more successful series of experiments has tricyclic acid for its starting point. The latter is converted by methyl alcohol and sulphuric acid into *methyl tricyclenate*, m. p.  $38^{\circ}$ , b. p.  $99^{\circ}$  (corr.)/14 mm.,  $D_4^{42.6}$  1.0255,  $n_D^{42.6}$  1.46953, which is reduced by sodium and alcohol to *tricyclol*, colourless needles, m. p.  $111$ — $112^{\circ}$  (corr.), b. p.  $141^{\circ}$ /71 mm. (*phenylurethane*, long, slender needles, m. p.  $92$ — $93^{\circ}$  [corr.]; *tricyclyl chloride*, b. p.  $85$ — $88^{\circ}$ /14.5 mm.,  $81$ — $82.5^{\circ}$ /11 mm.). The alcohol is converted by chromic acid in acetic acid solution into *tricyclal*, b. p.  $113$ — $115^{\circ}$ /31 mm., the smooth conversion of which into tricyclic acid shows that the carbon skeleton has been unchanged up to this point (*tricyclalsemicarbazone* forms small, matt needles, m. p.  $219$ — $220^{\circ}$  [decomp.]). *Tricyclalazine*, prisms or cubes, m. p.  $171$ — $172^{\circ}$  (corr.), is prepared by the action of hydrazine hydrate on the aldehyde, and is converted by an excess of hydrazine into the *monohydrazone*, which could not be obtained in the pure condition; the crude product was therefore directly heated at  $180$ — $195^{\circ}$  with a solution of sodium in alcohol, whereby it was almost quantitatively transformed into tricyclicene, mixed, however, with small quantities of an unsaturated hydrocarbon, probably camphene. The latter can be removed by treatment with potassium permanganate in glacial acetic acid solution, thus yielding ultimately pure tricyclicene, b. p.  $151.6$ — $152^{\circ}$  (corr.)/736 mm., m. p.  $64$ — $65^{\circ}$ . The hydrocarbon is somewhat readily affected by potassium permanganate in warm glacial acetic acid solution, yielding tricyclic acid and a carbonyl compound; the formation of the former shows that the hydrazone fission has occurred in the normal manner, and also that the same ring system is common to tricyclicene and tricyclic acid. H. W.

**Croton Resin.** R. BOEHM (*Arch. exp. Path. Pharm.*, 1915, **79**, 138—154).—The optical activity of croton oil is due to a resin which is dissolved in it. On removing the resin from the oil by extraction with methyl alcohol, the oil becomes inactive. The optical rotation of a croton oil may therefore serve as an indicator of its resin content. This resin has already been described by Dunstan and Boole (*A.*, 1895, i, 680), but the author gives an improved method for its extraction. Croton resin is a practically colourless, light powder with no definite melting point. It becomes soft, but not liquid, at  $80$ — $90^{\circ}$ . It is sparingly soluble in water and soluble in all proportions in organic solvents with the exception of light petroleum. The mean iodine value is 76.98. The rotation of various samples ranged from  $[\alpha]_D + 49.96^{\circ}$  to  $+ 63.23^{\circ}$ . Discordant results were obtained on analysis and molecular-weight determinations of different samples; the formula  $C_{36}H_{54}O_9$  and mol. wt. 627 are suggested with reservation. An attempt to throw some light on the constitution of the compound failed. The pharmacological activity of the resin is similar to that observed previously with croton oil. S. S. Z.

**Synthesis and Constitution of Anemonin.** Y. ASAHINA and A. FUJITA (*J. Pharm. Soc. Japan*, 1920, **455**, 1).—The chief results of this investigation may be summarised as follows: The sharp, oily substance volatile with steam obtained from *Ranunculus scleratus* L., consists in the main of the parent substance of anemonin, and has been given the name *protoanemonin*, which under spontaneous union of 2 mols. passes into anemonin. The synthesis of protoanemonin (V) was effected in the following manner: Lævulic acid (I) is converted into  $\beta$ -bromolævulic acid (II), and the latter acetylated; the resulting acetyl derivative (III) in anhydrous ether is digested with anhydrous sodium acetate, the acetylacetoacrylic acid (IV) doubtless formed thereby yielding on distillation a strongly vesicant oil protoanemonin, which on stirring quickly changes into anemonin (VI), m. p. 158°. Anemonin



was also prepared, but in poorer yield, by similar treatment of dibromoangelicalactone. Owing to the unpleasant physiological action of ranunkel-oil, an attempt was made to convert it into dihydroanemonin (IX). The latter could not be isolated in a pure condition, but was characterised by means of its semicarbazone, m. p. 185°, identical with the semicarbazone of lævulic acid,  $\text{CH}_3\cdot\text{C}(\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2)\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ . Anemonin is thus shown to be a dimeric product of protoanemonin and is constituted in accordance with the formula (VIII), whilst tetrahydroanemonin and dihydroanemonin have the constitutions represented by (VII) and (IX) respectively.



CHEMICAL ABSTRACTS.

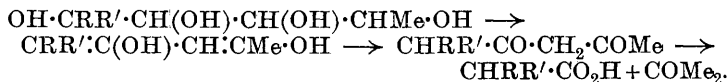
**Colloid Chemical Studies on the Acids of Hop Bitters.** H. LÜERS and A. BAUMANN (*Kolloid Zeitsch.*, 1920, **26**, 202—212).—The properties of the acid of hop bitters, both in aqueous solution and in wort, have been investigated by means of the change in surface tension which this substance brings about. Humulon ( $\alpha$ -hop

bitter acid) exists in the form of an hydrosol as a typical colloid-disperse system with a negative charge and in character intermediate between a suspensoid and an emulsoid. It is coagulated by heavy metals and is further dispersed by salts of the alkali metals. The presence of anions changes the surface tension of the solutions in the order chlorion < thiocyanate ion < iodion < sulphion < tartration. The humulon hydrosol changes its dispersity spontaneously with time in the sense that the particles become larger with a simultaneous increase in the surface tension. In acid solutions, the surface tension is smallest, the bitter taste least pronounced and the turbidity greatest, whilst in alkaline solution the reverse is the case. Emulsions exercise a dispersing action on humulon hydrosol; this is particularly the case with gelatin, which differs from the other emulsoids in causing a large reduction of the surface tension of solutions of the humulon hydrosol. Hand in hand with the change in the dispersity, a very marked stabilising of the sol occurs. Humulon is strongly adsorbed by charcoal from aqueous solution, but less strongly from solutions of sodium potassium tartrate. With decreasing dispersion, the adsorption of humulon increases. The concentration of the sol and the surface tension of the solution follow a parabolic equation of the same form as the adsorption law. The power of humulon to form a stable foam is in keeping with its power of reducing surface tension and its adsorption. The changes which occur in humulon on boiling are considered in connexion with the processes occurring in brewing.

J. F. S.

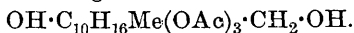
### **Hyptolide, a Bitter Principle of *Hyptis pectinata*, Poit.**

K. GORTER (*Bull. Jard. bot. Buitenzorg*, 1920, [iii], 1, 327—337). —The leaves of this Labiate are extracted with 95% alcohol; an equal volume of water is added, and after filtering off the chlorophyll, the filtrate is concentrated until there crystallises *hyptolide*,  $C_{15}H_{26}O_8$ , colourless needles, m. p.  $88.5^\circ$ ,  $[\alpha]_D^{20} + 6.75^\circ$ . Yield, 2% of the leaves. The substance dissolves in 50 parts of boiling water and readily in most organic solvents; it distils unchanged under reduced pressure. It contains a lactone group (hence the name) and three acetyl groups. After oxidation with silver oxide in alkaline solution and hydrolysis, four equivalents of acetic acid are liberated, the fourth one resulting apparently from the oxidation of a terminal group  $-CH(OH)\cdot CH_3$ . This group is eliminated to some extent as acetone by steam distillation with 10% sodium hydroxide, when at the same time an additional carboxyl group is generated. The mechanism of this reaction is represented as follows, where the group R contains the preformed carboxyl of the lactone,



Reduction in alcoholic solution with hydrogen and palladium

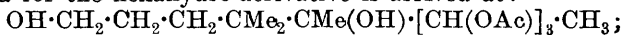
chloride introduces six atoms of hydrogen, transforming the compound  $C_{10}H_{14}Me(OAc)_3 \cdot \begin{smallmatrix} CO \\ \diagup \diagdown \\ O \end{smallmatrix}$  into an oil,



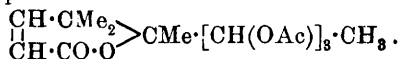
The latter contains three acetyl groups, but no lactone grouping; on boiling with acetic anhydride, one of the hydroxyl groups is eliminated as water, the other is acetylated; the resulting tetra-acetyl derivative is an oil.

Oxidation of hexahydrohptolide with potassium permanganate in alkaline solution gives one-third of its weight as a mixture of acids; from water there first crystallises a dibasic acid,  $C_9H_{16}O_4$ , needles, m. p. 130—131°, soluble in 180 parts of water at 26°, dissociation constant,  $4.2 \times 10^{-5}$ . The residue from the mother liquor of this acid was esterified, the ester was distilled, and after hydrolysis yielded  $\alpha\alpha$ -dimethylglutaric acid,  $C_7H_{12}O_4$ . Hence it is concluded that the acid  $C_9H_{16}O_4$  must be either  $\alpha\beta\beta$ - or  $\alpha\alpha'\alpha'$ -trimethyladipic. The latter acid is known and melts at 115°, so that the acid from hexahydrohptolide is considered to be identical with the former.

Oxidation of hexahydrohptolide with nitric acid (D 1.2) on the water bath also yields a small quantity of this supposed  $\alpha\beta\beta$ -trimethyladipic acid, together with succinic acid. The following formula for the hexahydro-derivative is arrived at:



and for the hptolide itself:



G. B.

**Reduction of Elsholtzia Ketone [Elsholtzione].** MICHIZO ASANO (*J. Pharm. Soc. Japan*, 1919, **454**, 999—1006).—

Elsholtzione,  $CH_2Pr^\beta \cdot CO \cdot C \begin{smallmatrix} CMe \cdot CH \\ \diagup \diagdown \\ O \end{smallmatrix}$  (A., 1915, i, 430), the reduction of which by the Clemensen and the Sabatier and Senderens methods has been unsuccessfully attempted by Asahina and his co-workers, is reduced by heating in a sealed tube with sodium ethoxide and hydrazine sulphate to 3-methyl-2-isoamylfuran, b. p. 172°/atm. or 78—79°/25 mm.,  $D_4^{20}$  0.8814,  $n_D^{19}$  1.45178. This substance is not identical with dihydroperillen (b. p. 182°,  $D_4^{20}$  0.8852,  $n_D^{20}$  1.45762); consequently, the positions of the two substituents in perillen,  $CH_2 \cdot CMe \cdot CH_2 \cdot CH_2 \cdot C_4H_7MeO$ , are still undetermined.

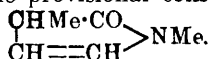
CHEMICAL ABSTRACTS.

**8-Hydroxy-2:3-quinoxanthone.** HARRY FITZGIBBON DEAN and MAXIMILIAN NIERENSTEIN (*T.*, 1920, **117**, 802—806).

**An Alkaloid in the Toxin of *Bufo vulgaris*.** HANS HANDOVSKY (*Arch. Exp. Path. Pharm.*, 1920, **86**, 138—159).—The aqueous extract of the toxin from *Bufo vulgaris* after being freed from the colloid it contains was treated with chloroform in order to



remove the bufotalin, and was precipitated with phosphotungstic acid in the presence of sulphuric acid. The precipitate was again brought into solution by various methods which are described, and extracted with ether. Some anhydrous oxalic acid was then added to the dehydrated ethereal extract, when the new alkaloid, *bufotenine*, crystallised as its oxalate,  $(C_6H_9ON)_2 \cdot C_2H_2O_4$ . The author adduces evidence for the provisional constitution



S. S. Z.

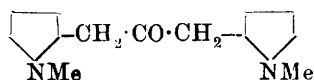
**Cinchona Alkaloids. III. Nitro- and Amino-sulphonic Acids, Nitro- and Amino-bases of some Hydrogenated Cinchona Alkaloids.** G. GIEMSA and J. HALBERKANN (*Ber.*, 1920, 53, [B], 732—750. Compare A., 1919, i, 342).—The hydrogenated alkaloids under investigation are smoothly converted by concentrated sulphuric acid and the calculated quantity of nitric acid (D 1.4) or nitrate into crystalline nitro-sulphonic acids, which are easily hydrolysed by warm 25% hydrochloric acid, and thus particularly adapted to the preparations of the pure nitro-bases. They are readily reduced to the corresponding amino-sulphonic acids by ferrous sulphate in the presence of alkali, and this behaviour is of the greater importance, since the amino-bases are not readily sulphonated. The amines themselves are smoothly obtained by hydrolysis of the aminosulphonic acids. The introduction of the nitro-group is found to increase the negative specific rotation of the compounds, whilst the amino-group displaces the rotation in the dextro-direction; the latter tendency is strengthened by the introduction of the sulphonic radicle to such an extent that amino-hydroquininesulphonic acid is dextrorotatory.

The following individual compounds are described: 5-Nitrohydrocupreinesulphonic acid,  $C_{19}H_{23}O_7N_3S$ , coarse, golden-yellow prisms, which gradually become green on exposure to sunlight and darken at  $205^\circ$ , and completely decompose, without melting, above  $245^\circ$ . 5-Nitrohydroquininesulphonic acid, anhydrous, yellow needles, which are sensitive to light and decompose above about  $250^\circ$ ,  $[\alpha]_D^{20} - 172.4^\circ$  (in alcohol),  $-186.7^\circ$  (in alcohol and 10% aqueous ammonia). 5-Nitroethylhydrocupreinesulphonic acid, yellow, prismatic needles, sensitive to light and decomposing above about  $270^\circ$ . Nitrohydrocinchoninesulphonic acid, yellow, microscopic platelets or cubes or prismatic rods ( $+H_2O$ ), thin, rectangular plates ( $+2H_2O$ ), m. p. (anhydrous)  $236^\circ$  (decomp.). Nitrohydrocinchonidinesulphonic acid, pale yellow, four-sided platelets, decomposing above ca.  $270^\circ$ . Nitrohydrocupreine,  $C_{19}H_{23}O_4N_3$  (from the sulphonic acid and hydrochloric acid [D 1.126]), coarse, red crystals, m. p.  $192^\circ$  (decomp.) after darkening at about  $180^\circ$ . 5-Nitrohydroquinine, pale yellow, anhydrous crystals, which are alkaline towards litmus, m. p.  $210$ — $212^\circ$  (decomp.) (the monosulphate, golden-yellow prisms [ $+15H_2O$ ] and the disulphate, yellow, amorphous powder [ $+2H_2O$ ], are described). 5-Nitroethylhydrocupreine, almost colourless, anhydrous leaflets, m. p.  $221$ — $223^\circ$  (decomp.),  $[\alpha]_D^{20} - 250.4^\circ$  in alcohol,  $-222.1^\circ$  in chloroform. Nitrohydro-

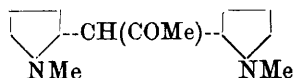
*cinchonine*, coarse, pale yellow, anhydrous plates, m. p. 234—235° (decomp.),  $[\alpha]_D^{20} + 163^\circ$  in alcohol,  $+161.8^\circ$  in chloroform. *Nitrohydrocinchonidine*, yellow, crystalline powder, m. p. 148° (decomp.),  $[\alpha]_D^{20} - 65.2^\circ$  in alcohol,  $-60.4^\circ$  in chloroform. *5-Aminohydroquininesulphonic acid*, yellow, anhydrous needles, m. p. about 227° (decomp.) after darkening at about 218°, or coarse, yellow prisms ( $+3\text{H}_2\text{O}$ ),  $[\alpha]_D^{20} + 18.85^\circ$  in absolute alcohol,  $+15.8^\circ$  in a mixture of alcohol and aqueous ammonia (the monosulphate, reddish-brown needles [ $+3\text{H}_2\text{O}$ ] or yellowish-red, amorphous powder [ $+ \text{H}_2\text{O}$ ], is described). *5-Aminoethylhydrocupreinesulphonic acid*, pale yellow needles ( $+ \text{H}_2\text{O}$ ), which become anhydrous and intensely reddish-brown when preserved over sulphuric acid. *Aminohydrocinchoninesulphonic acid*, almost colourless, coarse, anhydrous needles, m. p. 276° (decomp.). *Aminohydrocinchonidinesulphonic acid*, practically colourless, anhydrous needles, m. p. 282° (decomp.). 5-Aminohydroquinine (by hydrolysis of the aminosulphonic acid or reduction of the corresponding nitro-derivative by ferrous sulphate), yellow needles, m. p. 216—218°,  $[\alpha]_D^{20} - 19.99^\circ$  in absolute alcohol,  $-120.9^\circ$  in ether (the sulphate, yellowish-red crystals [ $+5\text{H}_2\text{O}$ ], is described). 5-Aminoethylhydrocupreine, from the aminosulphonic acid or the corresponding nitro-compound, m. p. 212°,  $[\alpha]_D^{20} - 16.98^\circ$  in alcohol,  $-123.8^\circ$  in ether, identical with the base prepared previously (*loc. cit.*) from the azo-compound. *Aminohydrocinchonine*, yellow, prismatic plates or colourless needles, according to the solvent used for crystallisation, m. p. 247°,  $[\alpha]_D^{20} + 204^\circ$  in absolute alcohol. *Aminohydrocinchonidine*, colourless needles, m. p. 170°, to a yellow liquid,  $[\alpha]_D^{20} - 80.7^\circ$  in absolute alcohol. H. W.

### Hygrine Alkaloids. III. Constitution of Cuskhygrine.

**Conversion of Cuskhygrine into Hygrine.** KURT HESS and HEINRICH FINK (*Ber.*, 1920, 53, [B], 781—809. Compare A., 1913, i, 1378; 1914, i, 199).—Cuskhygrine has been isolated by

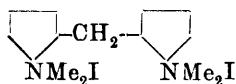


Liebermann from the liquid mixture of bases obtained in the preparation of cocaine, and on account of its empirical composition and its oxidation to hygric acid (1-methylpyrrolidine-2-carboxylic acid) has been assigned the annexed formula, in which, however, the symmetrical arrangement and the presence of the second pyrrolidine ring cannot be regarded as proved. The authors now bring definite evidence to show the presence of the carbonyl group, but find that cuskhygrine does not condense with benzaldehyde, oxalic ester, or amyl nitrite, and hence does not contain the active methylene group which the above formula indicates. Further examination leads them to



assign the constitution shown by the annexed formula to the base, the most important evidence for which is founded on the observations of Traube on the action of nitric oxide on ketones in the

presence of sodium ethoxide. Under these conditions, one molecule of cuskhygrine invariably absorbs six molecules of the gas. The primary additive product was too unstable to permit its isolation, but, on hydrolysis, yielded the sodium compound of methylenediisonitroamine,  $\text{CH}_2(\text{N}_2\text{O}_2\text{Na})_2$ ; the latter can only result from the presence of a methyl group, and accounts for the absorption of four molecules of nitric oxide. Since, according to Traube, a methylene group reacts more readily than the methyl radicle, it follows that such a group cannot be present in cuskhygrine, and that the absorption of the two remaining molecules of the gas is due to the presence of a methine group. Further products of the fission of cuskhygrine isonitroamine are 1-methyl-2-pyrrolidylacetic acid and a non-homogeneous, basic oil, which, after hydrogenation and treatment with sodium methoxide and methyl iodide, gives a uniform biquaternary iodide (annexed formula), thus affording convincing proof of the presence of a second pyrrolidine ring. Additional evidence in favour of the newer formula is also provided by the isolation of two isomeric hydrazones, which is impossible if the constitution assigned by Liebermann be accepted.



Cuskhygrine, b. p. 169—170°/23 mm., is converted by hydroxylamine into the corresponding *oxime*, flat pyramids, m. p. 53—54°, which does not undergo the Beckmann transformation when treated with phosphorus pentachloride, glacial acetic-hydrochloric acids, or sulphuric acid. The *semicarbazone* is a non-crystalline syrup. *Cuskhygrine- $\alpha$ -hydrazone*, colourless, syrupy oil, which has a marked tendency towards polymerisation, b. p. 182—183°/14 mm., is obtained in quantitative yield by the action of hydrazine hydrate on an alcoholic solution of the base; in addition to this substance, *cuskhygrine- $\beta$ -hydrazone*, b. p. 119—120°/15 mm., was obtained when (and only when) an old and somewhat decomposed specimen of hydrazine hydrate was used. The  $\alpha$ -hydrazone is only converted by sodium ethoxide to a relatively small extent into the corresponding *amine*, b. p. ca. 125°/16 mm., which gives a *picrate*, long needles, m. p. 185°; the  $\beta$ -hydrazone, on the other hand, yielded a *product*, b. p. 95—99°/20 mm., the *picrate* of which was found to be identical with that of di-1-methyl-2-pyrrolidylmethane (see later).

The products of the action of nitric oxide on cuskhygrine, and subsequent hydrolysis of the primary compound, were isolated in the following manner: (i) Methylenediisonitroamine was identified as the crystalline barium salt,  $\text{CH}_2\text{O}_4\text{N}_4\text{Ba} \cdot 3\text{H}_2\text{O}$ , which was further characterised by conversion into the silver salt and the dimethyl ester, m. p. 134°. (ii) 1-Methyl-2-pyrrolidylacetic acid was converted into its *ethyl* ester, colourless oil with basic, aromatic odour, b. p. 89—90°/15 mm. (*picrate*, prisms, m. p. 113°; *methiodide*, coarse, prismatic needles, m. p. 105—106° after slight previous softening), and the latter was hydrolysed by aqueous barium hydroxide to 1-methyl-2-pyrrolidylacetic acid, colourless crystals, which are very susceptible to the action of air, m. p. 95° (the m. p. is

given with reserve, as a suitable solvent for recrystallisation of the acid has not been found). (iii) The basic constituents were separated into two fractions, of which that of higher b. p. consisted of unchanged cuskhygrine, whilst that of b. p. 90—98°/16 mm. was found to be composed of a mixture of bases, which could not be separated by distillation. It did not yield a crystalline picrate, and was therefore hydrogenated in the presence of colloidal platinum. The mixture of saturated bases, b. p. 99—109°/16 mm., yielded a picrate, which gradually became completely solid, and, after repeated crystallisation, gave a pure specimen of di-1-methyl-2-pyrrolidylmethane picrate, m. p. 203° (see above). The action of formaldehyde and formic acid on the hydrogenated bases (which thus consist of a mixture of partly demethylated and methylated di-1-methyl-2-pyrrolidylmethanes) did not give a homogeneous product, but a more successful result was obtained by exhaustive methylation with sodium methoxide and methyl iodide, whereby the 1:1'-dimethiodide of di-1-methyl-2-pyrrolidylmethane was prepared in cubic crystals, m. p. 200° after slight previous softening; it was further characterised by converting it, by means of silver chloride, into the methochloride, and transformation of the latter into the aurichloride, canary-yellow, microcrystalline powder, which decomposed at 260°.

When an ethereal solution of cuskhygrine is allowed to remain for a considerable time in contact with solid potassium hydroxide, the base undergoes a partial conversion into *r*-hygrine (the picrate of the latter has m. p. 149—150°, instead of 174° [corr.], after softening at 160°, as previously recorded), brown, viscous products being simultaneously formed. A similar change is observed when cuskhygrine is boiled for some time with aqueous-alcoholic potassium hydroxide solution.

H. W.

**Pelletierine and Methylpelletierine.** GEORGES TANRET (*Compt. rend.*, 1920, **170**, 1118—1120).—The author reaffirms his results as to the properties of the two alkaloids, pelletierine and methylpelletierine, found in the bark of the pomegranate tree (compare A., 1880, 481), and refutes the statements of Hess and Eichel (compare A., 1917, i, 349; 1918, i, 33, 34) as to the non-existence of optically active forms of these alkaloids. Certain salts are described.

Pelletierine,  $[\alpha]_D - 31.1^\circ$ , gives a *sulphate*, m. p. 133°,  $[\alpha]_D - 30.3^\circ$ ; a *hydrochloride*, m. p. 145°,  $[\alpha]_D - 41.2^\circ$ ; a *hydrobromide*, m. p. 137°,  $[\alpha]_D - 32.5^\circ$ ; a *nitrate*, m. p. 82—85°,  $[\alpha]_D - 34.8^\circ$ ; a *picrate*, m. p. 131—133°; a *platinichloride*, m. p. 214—216°; a *silicotungstate*; an *acetyl* derivative, b. p. 205—210°/40 mm.,  $[\alpha]_D + 32.6^\circ$ ; a *benzoyl* derivative,  $[\alpha]_D + 18.7^\circ$ ; and a *semicarbazone hydrochloride*, m. p. 168—170°,  $[\alpha]_D - 10.8^\circ$ . Pelletierine is very sensitive to heat and to acids and bases, rapidly losing its optical activity.

Methylpelletierine, b. p. 106—108°/45 mm.,  $[\alpha]_D + 27.7^\circ$ , and in aqueous solution  $+ 24.1^\circ$ , gives a *hydrochloride*, m. p. 168—170°,

$[\alpha]_D + 41.2^\circ$ ; a *hydrobromide*, m. p.  $165-167^\circ$ ,  $[\alpha]_D + 33.5^\circ$ ; a *sulphate*,  $[\alpha]_D + 38^\circ$ ; a *picrate*, m. p.  $157-159^\circ$ ; and a *platini-chloride*, m. p.  $206-208^\circ$ .  
W. G.

**The Chemical Isolation of Vitamines.** C. N. MYERS and CARL VOEGTLIN (*J. Biol. Chem.*, 1920, **42**, 199—205).—Autolysed yeast filtrate is not a satisfactory product from which to attempt the isolation of the antineuritic vitamin. The active material is readily extracted from dried yeast by means of acidified methyl alcohol. From this fraction, an active, crystalline substance can be obtained by using Funk's silver acetate method, followed by mercuric sulphate precipitation. This substance becomes inactive on drying. The method eliminates purines, histidine, proteins, and albumoses. Stachydrine, trigonelline, and allied betaines show no antineuritic activity.  
J. C. D.

**Constitution of the Organic Nitrogen Bases of Californian Petroleum.** C. F. MABERY and L. G. WESSON (*J. Amer. Chem. Soc.*, 1920, **42**, 1014—1030).—A re-examination of the basic constituents of Californian petroleum (A., 1900, i, 533) has shown them to consist mainly of alkylated quinolines (or *isoquinolines*), with a small proportion of hydrogenated derivatives or pyridine compounds. By refractionation, the material was divided into fractions boiling over intervals of  $2-4^\circ$  covering a range of  $130-283^\circ/50-90$  mm. The analysis and mol.-wt. determination of one of these agreed with the formula of an alkylated quinoline,  $C_{15}H_{19}N$ , whilst from another an acid ferrocyanide, derived from the base,  $C_{13}H_{15}N$  was obtained. All the fractions yield pyridine pentacarboxylic acid and a methylpyridinetetracarboxylic acid when boiled with potassium permanganate solution, and therefore contain at least three alkyl groups, of which the relatively simple nature is shown by the absence of propionic, or higher fatty, acid from the oxidation products. 3-Methylquinoline was obtained by distilling with lime the chromic acid oxidation product of one fraction of base. A medium fraction yielded a phthalone derivative by condensation with phthalic anhydride. The bases are unchanged by nitrous acid, but can be reduced to secondary bases, from which nitroso-derivatives are obtainable. Thus, a product, b. p.  $208-210^\circ/90$  mm.,  $C_{14}H_{20}N$  or  $C_{14}H_{21}N$ , was obtained from a fraction  $C_{14}H_{17}N$ . Unsuccessful attempts were made to break down the pyridine ring of the benzoylated reduction product by means of phosphorus pentachloride. Definite picrates, platini-chlorides, or double mercury salts could not be obtained from any fraction, probably because these, although representing a fairly satisfactory separation of the bases as regards molecular weight, are nevertheless mixtures containing small proportions of the other components previously mentioned. A lower fraction underwent sulphonation with fuming sulphuric acid, whilst a medium one was resistant to this agent. The action of bromine, iodine, hydriodic acid, and nitric acid is also described.  
J. K.

**A New Series of Nitrogenous Compounds obtained from Camphoroxalic Acid.** PERCY CHORLEY and ARTHUR LAPWORTH (T., 1920, 117, 728—742).

**The Addition of 1:3-Diketones to Thiocarbimides. I. Acetylacetone and certain Aryl Thiocarbimides.** DAVID E. WORRALL (*J. Amer. Chem. Soc.*, 1920, **42**, 1055—1061).—Acetyl-

acetone, in the form of its sodium salt, reacts at the ordinary temperature with thiocarbimides with formation of thioanilides. The acetyl group is removed from these compounds by solution in cold alkali hydroxide, and acidification at 0° after some hours. Both the resulting, and the original, thioanilides give the same products, and react very easily with phenylhydrazine and with hydroxylamine, phenylhydrazones and isooxazoles being respectively produced, with elimination of the sulphur atom. *Thiodiacetoacetyl-anilide*,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{CS}\cdot\text{NHPh})\cdot\text{CO}\cdot\text{CH}_3$ , yellow needles, m. p. 107—108°, and *thioacetoacetylanilide*,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CS}\cdot\text{NHPh}$ , yellow plates, m. p. 63·5—64°, each give the phenylhydrazone of thioformanilide when treated with phenylhydrazine, and with

hydroxylamine, 3-*anilino-5-methylisooxazole*,  $\text{O} \begin{array}{c} \text{CMe}\cdot\text{CH} \\ \diagdown \\ \text{N}=\text{C}\cdot\text{NHPh} \end{array}$ , needles, m. p. 111—112°.

*Thiodiacetoacetyl-p-toluidide*,  $\text{CHAc}_2\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , yellow plates, m. p. 132—133°; *thioacetoacetyl-p-toluidide*,  $\text{CH}_2\text{Ac}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , yellow needles, m. p. 68—69°; 3-*p-tolu-*

*idino-5-methylisooxazole*,  $\text{O} \begin{array}{c} \text{CMe}\cdot\text{CH} \\ \diagdown \\ \text{N}=\text{C}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me} \end{array}$ , needles, m. p. 122—124°; *thiodiacetoacetyl-p-bromoanilide*,

$\text{CHAc}_2\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br}$ , needles, m. p. 137—139°; *thioacetoacetyl-p-bromoanilide*,  $\text{CH}_2\text{Ac}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br}$ ,

m. p. 110—111°; 3-*p-bromoanilino-5-methylisooxazole*,

$\text{O} \begin{array}{c} \text{CMe}\cdot\text{CH} \\ \diagdown \\ \text{N}=\text{C}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br} \end{array}$ , needles, m. p. 178—180°; *thiodiacetoacetyl-m-toluidide*, yellow plates, m. p. 124—125°; *thiodiacetoacetyl-o-toluidide*, yellow plates, m. p. 126·5—128°.

J. K.

**Preparation of an Arylcarbamide Chloride.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 318237; additional to D.R.-P. 241822; from *Chem. Zentr.*, 1920, ii, 691).—*p*-Nitroaniline (in place of  $\beta$ -aminoanthraquinone) is treated with carbonyl chloride until the amine hydrochloride has completely disappeared with the object of preparing *p*-nitrophenylcarbamide chloride [*p*-nitrophenylcarbamy] chloride]; the temperature is below that at which the latter is converted into the corresponding carbimide. When carbonyl chloride is passed into a cooled suspension of *p*-nitroaniline in toluene, a mixture of *p*-nitrophenylcarbamy] chloride and nitroaniline hydrochloride is first produced; at the ordinary or slightly higher temperature, the latter is converted into

the carbamyl chloride, hydrogen chloride being evolved. The pure substance is a valuable intermediate product in the preparation of carbamide derivatives, and, for example, is quantitatively transformed by a solution of aniline in benzene into *p*-nitrodiphenylcarbamide.

H. W.

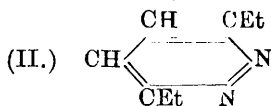
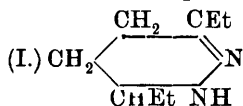
**Removal of Sulphur from Organic Compounds by means of Arsenic Trioxide.** WALTHER HERZOG (*Zeitsch. angew. Chem.*, 1920, **33**, I, 140).—Organic compounds containing sulphur may be readily desulphurised by treatment with arsenic trioxide. The method is particularly suitable for the preparation of carbodi-phenylimide from symmetrical diphenylthiocarbamide, which for the purpose is dissolved in xylene or other inert solvent and boiled with arsenic trioxide under reflux.

C. A. M.

**Orientation of the Nitro- and Arylazo-glyoxalines. Fission of the Glyoxalone Nucleus.** ROBERT GEORGE FARGHER (*T.*, 1920, **117**, 668—680).

**Action of Hydrazine on the Acyclic 1:4-Diketones.** E. E. BLAISE (*Compt. rend.*, 1920, **170**, 1324—1326).—Hydrazine acts on acetylacetone in hydrochloric acid solution to give a compound,  $C_{12}H_{20}N_4$ , m. p. 52—53°, which is probably a dimeride of the dihydropyridazine expected.

In acetic acid solution hydrazine gives with *s*-dipropionylethane, diethyltetrahydropyridazine (I), b. p. 100°/15 mm., giving a benzoyl derivative, b. p. 210°/16 mm., and diethylpyridazine (II),



b. p. 121—122°/15 mm., giving a *platinichloride*, m. p. 180—182°, and a *picrate*, m. p. 108—109°.

W. G.

**New Type of Diisonitroso-peroxides.** E. J. VIRGIN (*Diss. Upsala*, 1914, pp. 63).—1:2:4:5-Tetraketo-3:6-dibenzoyl-4:5-dihydropyridazine [4:5-diketo-3:6-dibenzoyl-4:5-dihydropyridazine

1:2-dioxide] (A),  $\begin{array}{c} \text{NO:CBz}\cdot\text{CO} \\ | \\ \text{NO:CBz}\cdot\text{CO} \end{array}$ , red crystals exploding at 105—110°

in a capillary tube, is obtained by warming  $\alpha\gamma\delta\zeta$ -tetraketo- $\alpha\zeta$ -diphenylhexane with nitrogen peroxide and ether at 25—27° for twenty minutes; it does not respond to the Liebermann nitroso-reaction. The mother liquors contain a small quantity of the substance O (see below). 1:5-Dihydroxy-2:4-diketo-3:6-dibenzoyl-1:4-dihydropyridazine [1:5-dihydroxy-4-keto-3:6-dibenzoyl-1:4-dihydropyridazine 2-oxide] (B), obtained from A by reduction in cold acetone with hydriodic acid (4 mols.) and a saturated solution of sulphur dioxide or with saturated hydrobromic acid, separates from acetone in pale yellow needles, m. p. 128° (decomp.), forms a *disodium* salt, develops a deep red coloration with ferric chloride in acetone solution, yields a *diacetyl* derivative, yellow needles, m. p. 160° (decomp.), and is reconverted into A by bromine

or nitrogen peroxide in ether or chloroform or by nitrous acid in ether. 1:5-Dihydroxy-4-keto-3:6-dibenzoyl-1:4-dihydropyridazine (C), obtained by keeping B with ice-cold acetic acid saturated with hydrogen iodide for two hours at the ordinary temperature and then adding a saturated solution of sulphur dioxide, separates from alcohol in anhydrous, yellow crystals, m. p. 181—182°, or as a hydrate, yellow, microscopic needles and prisms, decomp. 125°; with ferric chloride in alcohol and acetone it develops an intense red coloration, which changes through green to violet by the addition of water.  $\epsilon$ -Chloro- $\beta$ -oximino- $\alpha\gamma\delta\zeta$ -tetraketo- $\alpha\zeta$ -diphenylhexane (D), obtained by treating an acetone solution of A with concentrated hydrochloric acid, crystallises from a mixture of ether and benzene in rhombic plates containing 1 mol.  $C_6H_6$ , develops a coloration with ferric chloride, and forms a diacetyl derivative, prisms, m. p. 156—157°. 3-Chloro-1:5-dihydroxy-4-keto-6-benzoyl-1:4-dihydropyridazine (E), obtained together with its isomeride F (below) by saturating a solution of B in 80% alcohol with hydrogen chloride at 0° and adding ether after concentration, forms yellow blades, m. p. 190° (decomp.). 6-Chloro-1:5-dihydroxy-4-keto-3-benzoyl-1:4-dihydropyridazine (F) separates from the alcoholic mother liquor in yellow crystals, m. p. 180°. 1:5-Dihydroxy-4-keto-6-benzoyl-1:4-dihydropyridazine (G), obtained by treating E with hydriodic acid, forms yellowish-brown plates, m. p. 245° (decomp.). 4:5-Dihydroxy-6-benzoylpyridazine (H), yellowish-white crystals, m. p. 239—240° (slight decomp.), is obtained from G in a similar manner. 1:5-Dihydroxy-4-keto-6-benzyl-1:4-dihydropyridazine (I), needles, m. p. 261° (decomp.), is obtained by warming G with a solution of hydrogen iodide in acetic acid; the mother liquor, after being neutralised, yields 4:5-dihydroxy-6-benzylpyridazine (J), m. p. 252—253° (decomp.), which can also be prepared from H, I, and K.

3-Chloro-4:5-dihydroxy-6-benzoylpyridazine (K), rectangular plates, m. p. 232—233°, is obtained by treating F for thirty minutes with an acetic acid solution of hydrogen iodide. 4:5-Dihydroxy-6-benzoyl-3-benzylpyridazine (L), pale yellow, rectangular prisms, m. p. 229—230° (monoacetyl derivative, yellow prisms, m. p. 189—190°), is obtained by boiling C with the same reagent. By heating C with this reagent in a sealed tube for five hours, 4:5-dihydroxy-3:6-dibenzylpyridazine (M), plates, m. p. above 300° (monoacetyl derivative, plates, m. p. 215°; diacetyl derivative, prisms, m. p. 147°), is obtained.  $\beta\epsilon$ -Dioximino- $\alpha\gamma\delta\zeta$ -tetraketo- $\alpha\zeta$ -diphenylhexane (N), obtained by boiling B with acetone, forms thin prisms, m. p. 126° (decomp.), yields oximinobenzoylacetic acid,  $CO_2H \cdot CBz \cdot NOH$ , irregular prisms, m. p. 130° (decomp.), by treatment with sulphuric acid and acetone, and is converted into A and a small quantity of O by treatment with nitrogen peroxide in ethereal solution; it forms a diacetyl derivative, yellow crystals, m. p. 166°. By treatment with hydrogen chloride in acetic acid N is converted into an isomeride (O), the diacetyl derivative of which has m. p. 186—187°.



3:5-Dibenzoyl-1:2:4-oxadiazole,  $\text{CBz} \begin{smallmatrix} \text{N} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{CBz} \end{smallmatrix}$ , six-sided plates, m. p.  $105^\circ$ , obtained by keeping A in methyl-alcoholic solution for twenty-four hours, forms a diphenylhydrazone, yellow needles, m. p.  $171-172^\circ$ . Ethyl 1:2:4:5-tetraketo-4:5-dihydropyridazine-3:6-dicarboxylate [ethyl 4:5-diketo-4:5-dihydropyridazine-3:6-dicarboxylate 1:2-dioxide], m. p.  $70^\circ$ , is obtained from ethyl ketipinate and nitrogen peroxide in ethereal solution at  $-15^\circ$ .

The dioximino-peroxides of ethyl acetonedicarboxylate are discussed, and reasons for some types of its reactions are given, based on the behaviour of analogous compounds of A.

#### CHEMICAL ABSTRACTS.

**Bistetrazole.** E. OLIVERI-MANDALÀ (*Gazzetta*, 1920, **50**, i, 256—261. Compare A., 1913, i, 1398).—Bistetrazole exhibits great stability, and only by means of hot concentrated sulphuric acid or fused potassium hydroxide is its molecule profoundly decomposed. When treated with diazomethane in absolute ethereal solution, it yields, together with a small proportion of the dimethyl derivative, a compound which is isomeric with bistetrazole, but, unlike the latter, exhibits no acid characters; for this compound the structure  $\begin{smallmatrix} \text{N} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{N} \end{smallmatrix} > \text{CH} \cdot \text{CH} < \begin{smallmatrix} \text{N} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{N} \end{smallmatrix}$  is tentatively proposed.

Whereas concentrated sulphuric acid exerts oxidising and hydrolysing actions on bistetrazole, thus:  $\text{C}_2\text{H}_2\text{N}_8 + 2\text{H}_2\text{O} + \text{O} = 3\text{N}_2 + 2\text{CO}_2 + 2\text{NH}_3$ , fused potassium hydroxide decomposes it with formation of potassium azide, apparently in accordance with the equation  $\text{C}_2\text{H}_2\text{N}_8 \rightarrow 2\text{N}_3\text{H} + \text{C}_2\text{N}_2$ . This tendency to lose azoimide, manifested generally by cyclic compounds containing the grouping  $\cdot\text{N} \cdot \text{N} \cdot \text{NH} \cdot$ , is exhibited also by most compounds in which the triazo-group,  $\cdot\text{N} < \begin{smallmatrix} \text{N} \\ \parallel \\ \text{N} \end{smallmatrix}$ , occurs; only azides of the following structures

undergo decomposition with elimination of a molecule of nitrogen: (1)  $\cdot\text{CO} \cdot \dot{\text{C}}\text{H} \cdot \text{N}_3 \rightarrow \text{N}_2 + \cdot\text{CO} \cdot \dot{\text{C}}\text{NH}$ , and (2)  $\cdot\text{CH} \cdot \text{CO} \cdot \text{N}_3 \rightarrow \text{N}_2 + \cdot\text{CH} \cdot \text{CO} \cdot \text{N} \cdot \rightarrow \cdot\text{CH} \cdot \text{N} \cdot \text{CO}$ .

The cryoscopic behaviour of bistetrazole in aqueous solution confirms the marked ionisation of this compound indicated by conductivity measurements (*loc. cit.*). In freezing acetic acid the molecular weight is normal.

The isomeride of bistetrazole (see above) forms acicular aggregates of crystals, m. p.  $98-99^\circ$ , and is insoluble in alkali carbonate solution.

Dimethylbistetrazole,  $\text{C}_2\text{N}_8\text{Me}_2$ , forms crystals, m. p.  $150-160^\circ$ , and yields nitrogen and methylamine when treated with concentrated alcoholic potassium hydroxide. The sodium,  $\text{C}_2\text{N}_8\text{Na}_2$ , silver,  $\text{C}_2\text{N}_8\text{Ag}_2$ , barium,  $\text{C}_2\text{N}_8\text{Ba} \cdot 3\text{H}_2\text{O}$ , and copper,  $\text{C}_2\text{N}_8\text{Cu}$ , salts were prepared and analysed; the copper and mercury salts explode violently when heated.

T. H. P.

**The Structure and Properties of the Compound obtained by the Thermal Decomposition of *o*-Methoxyphenyl Benzylidenehydrazinocarboxylate.** OTTO DIELS and HEINRICH GRUBE (*Ber.*, 1920, **53**, [B], 854—863).—In a previous communication (A., 1914, i, 940) it has been shown that *o*-methoxyphenyl benzylidenehydrazinocarboxylate is smoothly decomposed, when heated, into guaiacol and a sparingly soluble, crystalline substance,  $(C_8H_6ON_2)_x$ ; the constitution of the latter is now shown to be represented by the formula  $CHPh:N \cdot N \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} N \cdot N : CHPh$ .

The compound is decomposed by protracted heating with a mixture of glacial acetic and fuming hydrochloric acids into benzylidenaurazine,  $CHPh:N \cdot N \begin{smallmatrix} \text{CO} \cdot NH \\ \diagup \quad \diagdown \\ \text{CO} \cdot NH \end{smallmatrix}$ , long, colourless needles, m. p. 254°, which is further decomposed by water into benzaldehyde and urazine, m. p. 270°. These reactions, however, throw but little light on the constitution of the substance, since the products could be equally well derived from a di- or tri-polymeride, discrimination between which cannot be effected by determination of the molecular weight on account of the very slight solubility of the substance. More information is afforded by its milder fission by means of phenylhydrazine in the presence of dimethylaniline, which gives rise to the compound,  $CHPh:N \cdot N \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} N \cdot NH_2$ , colourless, crystalline powder, m. p. 254—255°, and phenylbenzylidenehydrazine. The presence of a free amino-group in the former is shown by its conversion into a *monoformyl* derivative, shining crystals, m. p. 278°, and a *diacetyl* compound, colourless, pearly leaflets, m. p. 269°, as well as by its condensation with furfuraldehyde and anisaldehyde with the formation of *derivatives*,  $C_{14}H_{10}O_3N_4$ , pale brown prisms, which decompose without melting at 251° after darkening at 247°, and  $C_{17}H_{14}O_3N_4$ , colourless crystals, m. p. 272—273°, to a reddish-brown liquid after becoming yellow at 268°. The close relationship of the amine to the parent substance is shown by its re-conversion into the latter when boiled with benzaldehyde in dimethylaniline solution in an atmosphere of carbon dioxide. The amine or its formyl derivative is converted by boiling aqueous potassium hydroxide solution into dibenzylidenecarbohydrazide,  $CHPh:N \cdot NH \cdot CO \cdot NH \cdot N : CHPh$ , which when obtained in this manner forms small, canary-yellow leaflets, m. p. 198°; when, however, the compound is prepared by mixing alcoholic solutions of carbohydrazide and benzaldehyde in the usual manner, it is obtained in colourless leaflets. The same *formate*, colourless, silky, needles, m. p. 189—190°, with yellow coloration after softening at 187°, is obtained by the action of formic acid on either variety, and this is converted by alkali or by heat (with evolution of formic acid) into the yellow modification. Precisely similar observations with the *acetate* are recorded. Crystallographically, the modifications are identical with one another, and they also show the same

melting point since the colourless passes into the yellow variety when heated. H. W.

**Isomeric Phthalyhydrazides.** FREDERICK DANIEL CHATTAWAY and WILLIAM TESH (T., 1920, 117, 711—720).

**Action of Benzyl Alcohol on Albumins and Ferments.** J. JACOBSON (*Compt. rend. Soc. Biol.*, 1920, 83, 255—256; from *Chem. Zentr.*, 1920, i, 783).—Benzyl alcohol precipitates egg-albumin and peptone even from solutions containing one part in a million, and the precipitates do not redissolve in distilled water. Benzyl alcohol has a retarding action towards pepsin, pancreatin, the rennet ferment, the souring of milk, and brewer's yeast.

H. W.

**Temperature Sensitiveness of Saccharase (Invertase).** H. VON EULER and I. LAURIN (*Arkiv. Kem. Min. Geol.*, 1917, 7, No. 24, 1—30. Compare following abstract).—The temperature-coefficient of inversion by saccharase from yeast has been determined in solution of acidity  $P_H=4.5$ . The constant  $A$  of Arrhenius's temperature formula is found to be  $10500 \pm 500$  for the range  $0^\circ$  to  $20^\circ$ , and this can be taken as the inversion constant over this range. At temperatures  $20^\circ$  to  $52^\circ$ , a smaller value,  $8800 \pm 400$ , is obtained. The inactivation of yeast at the optimum acidity has been determined over the range  $50^\circ$  to  $65^\circ$ . Heating yeast for one hour at  $59^\circ$  reduces the activity of the saccharase by one half. The inactivation constant at this temperature is  $k_c = 5 \times 10^{-3}$ . For  $P_H=4.5$ , the Arrhenius formula applied to the inactivation gives a constant 101000. The inactivation of saccharase has been determined for  $P_H=3, 4, 5$ , and  $5.7$  over the range  $42^\circ$  to  $55^\circ$ , and it is shown that the minimum temperature sensitiveness lies at acidities  $P_H=4-5$ , that is, at the acidity of optimum enzyme activity. The Arrhenius constant is greatest in this region. The temperature sensitiveness of separated invertase is very little different from that in the yeast cells. The cell appears to exercise a slight protecting action, which allows the non-separated invertase to be heated to about  $1^\circ$  higher than the separated product. The inactivation temperature constant is a little greater for the separated invertase than for the non-separated. Invertase from bottom yeast has a smaller temperature sensitiveness than that from top yeast. The difference amounts to about  $2^\circ$ , that is, the invertase from bottom yeast can be heated  $2^\circ$  higher than that from top yeast. The greater stability of bottom yeast in comparison with top yeast is not due to the presence of a protecting substance in the former, because the addition of the liquid from bottom yeast to top yeast does not increase the stability of this substance. J. F. S.

**Influence of Temperature and Acidity on the Formation of Saccharase.** H. VON EULER and O. SVANBERG (*Arkiv. Kem. Min. Geol.*, 1917, 7, No. 23, 1—32).—The dependence of saccharase formation on the temperature and acidity has been investigated.

It is shown that for yeast a well-defined temperature optimum for saccharase formation lies between  $26^{\circ}$  and  $30^{\circ}$ , and that at  $35^{\circ}$  no further formation takes place. The saccharase formation is strongly dependent on the acidity of the solution. The maximum formation occurs practically at the same point as the maximum activity of the enzyme. At a greater acidity than  $P_H=2$ , a disturbance of the saccharase is noticed, but even at acidity  $P_H=6-7$  a strong enzyme formation occurs, which is about 90% of that observed under the best conditions of acidity. The saccharase content of fresh living yeast is not changed by ten hours' washing with water at  $10^{\circ}$ .  
J. F. S.

**Diphenylarsenious Chloride and Cyanide. (Diphenylchloroarsine and Diphenylcyanoarsine.)** GILBERT T. MORGAN and DUDLEY CLOETE VINING (T., 1920, 117, 777—783).

**Organo-derivatives of Bismuth. III. The Preparation of Derivatives of Quinquevalent Bismuth.** FREDERICK CHALLENGER and ARCHIBALD EDWIN GODDARD (T., 1920, 117, 762—773).

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## Physiological Chemistry.

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### **Liquid for Determining Specific Gravity of Blood.**

H. HARTRIDGE (*Proc. Physiol. Soc.*, 1920; *J. Physiol.*, 1920, **53**, lxxxiii).—Lyle's golden syrup made up with water to D 1·080 is a good substitute for the usual glycerol solution. A few c.c. of formalin solution should be added as a preservative. J. C. D.

**The Neutrality of the Blood.** W. M. BAYLISS (*J. Physiol.*, 1920, **53**, 162—179).—Intravenous injection of acid in sufficient quantity to neutralise half the bicarbonate in the blood does not increase the hydrogen-ion concentration of the plasma. The chief mode of compensation is by increase in pulmonary ventilation, and consequent decrease of the carbon dioxide of the blood. Renal excretion of acid, and ammonia production in the liver, do not appreciably come into play in short experiments. Injected alkali is not so readily neutralised. The chief agent in this case appears to be excretion of alkaline urine. The proteins of the plasma play no perceptible part in the maintenance of neutrality between the limits of hydrogen-ion concentration possible in the living organism, namely, below  $10^{-4}$  or above  $10^{-10}$  normal. No evidence was obtained that either sodium bicarbonate, serum proteins, or both together convey carbon dioxide from the tissues to the lungs. Thus the only function of the sodium bicarbonate in the blood is to regulate the hydrogen-ion concentration, whilst under normal conditions the only function of the proteins is to give a colloidal osmotic pressure and a moderate degree of viscosity

to the plasma. A simple method of determining the hydrogen-ion concentration of blood by means of indicators is described.

J. C. D.

**The Reaction and Carbon Dioxide-carrying Power of Blood.** I. T. R. PARSONS (*J. Physiol.*, 1919, **53**, 42—59).—By mathematical calculation, it is determined that a system composed of carbon dioxide and one other weak acid with a fixed total amount of sodium distributed between them has a carbon dioxide dissociation curve identical with that of blood. The proteins of the blood constitute the second weak acid, which shares with carbon dioxide the available sodium. The whole of the combined carbon dioxide of the blood is in the form of bicarbonate, but the proteins present in the blood confer on it a property which pure bicarbonate solution does not possess, namely, that of forming an efficient carrier for carbon dioxide. In the blood, the "availability" of the sodium is regulated by the proteins in such a way that the carbon dioxide tends to be expelled at lower tensions, so that an efficient transport of gas is brought about.

CHEMICAL ABSTRACTS.

**The Colloid-free Filtrate of Serum.** A. R. CUSHNY (*J. Physiol.*, 1920, **53**, 391—398).—When serum is filtered through collodion membranes, the filtrate contains most of the crystalloid components in the same proportions as in the original serum. The only exceptions are calcium and possibly magnesium, which pass the filter in a lower concentration. Therefore the non-colloid constituents, other than these two elements, are in simple solution in serum, whilst part of the calcium and magnesium is probably in some form of combination with the proteins.

J. C. D.

**Metabolism of Carbohydrates.** J. A. HEWITT and J. PRYDE (*Proc. Physiol. Soc.*, 1919; *J. Physiol.*, 1920, **53**, lxx; from *Physiol. Abstr.*, 1920, **5**, 79).—Experiments on the stereochemistry of certain carbohydrates in the alimentary canal indicate that the  $\alpha$ - and  $\beta$ -forms of glucose are not present in a simply equilibrated aqueous solution.

J. C. D.

**Nitrogenous Equilibrium and Absence of Vitamines.** A. DESGREZ and H. BIERRY (*Compt. rend.*, 1920, **170**, 1209—1211).—With a deficiency of vitamins, rats can be kept, for a certain time, in nitrogenous equilibrium for varying proportions of albumin, fats, and sugars, in a ration supplying sufficient energy. The minimum of albumin, fat, or sugar permissible is controlled by the chemical nature of the particular class of nutrient, and the ratio of the other two classes present. The minimum of nitrogenous nutrient necessary is reached when a sugar is present in sufficient amount in the ration.

W. G.

**Carotinoids and Fat-soluble Vitamine.** L. S. PALMER (*Science*, 1919, **50**, 1—2; from *Physiol. Abstr.*, 1920, **5**, 92).—The author disagrees with Steenbock's hypothesis as to the identity of carrotene and fat-soluble A. In many cases the relation breaks

down, and chickens have been raised to maturity on diets free from carotinoids. Further, certain oils (for example, cottonseed oil) are rich in carotinoids, but are destitute of the fat-soluble vitamine.

J. C. D.

**The Behaviour of Basic Bismuth Nitrate towards Dilute Acids.** P. W. K. BÖCKMANN (*Arch. Exp. Path. Pharm.*, 1916, **80**, 140—146).—Experiments were instituted with the object of ascertaining whether basic bismuth nitrate is capable of neutralising acids. To nitric acid of known concentration, basic bismuth nitrate was added in excess and shaken for a couple of days at 18°. The bismuth, as well as the total acid content of the filtrate, was then estimated. On the assumption that the bismuth was present in the filtrate as the normal salt, the free acid was calculated by difference. The H-ion concentration of the above filtrates was also determined colorimetrically. From the results obtained, it was concluded that at an acidity similar to that which prevails in the stomach, basic bismuth nitrate does not possess any neutralising capacity.

S. S. Z.

**The Effect of Injection of Guanidine on the Creatine-content of Muscle.** G. M. WISHART (*J. Physiol.*, 1920, **53**, 440—445).—Intravenous or subcutaneous injections of inorganic salts of guanidine cause an increase in the creatine content of muscles. The bearing of this observation on the theories of creatine formation is discussed.

J. C. D.

**The Formation of Adrenaline.** F. KNOOP (*Ber.*, 1920, **53**, [B], 716—718).—A further contribution to the controversy with regard to the mode of formation of adrenaline in the organism (compare Rosenmund and Dornsaft, this vol., i, 56, 327; Knoop, this vol., i, 161).

H. W.

**The Chemical Nature of the Bee's Poison.** FERDINAND FLURY (*Arch. Expt. Path. Pharm.*, 1920, **85**, 319—339).—The author carried out some investigations on the protein-free poison isolated by Langer from the poison sac of the bee. It was found that the principle was a base of complicated constitution. By means of digestive processes, a considerable fraction of a lipid nature was obtained from it. The following were the products of hydrolysis with hydrochloric acid: (1) a ring compound of the indole series; (2) choline; (3) glycerol; (4) phosphoric acid; (5) palmitic acid; (6) a high molecular, non-crystallisable, unsaturated fatty acid; (7) a volatile fatty acid, presumably butyric acid; (8) and a nitrogen-free fraction. The latter fraction was found to be the pharmacologically active principle of the bee's poison. According to the method of isolation, it can be obtained either as a neutral compound sparingly soluble in water or as an acid soluble in water. The author expresses the opinion that the bee's poison in the natural secretion is present as a complex compound in combination with lecithin and a basic fraction.

S. S. Z.

**The Nature of Excreted Arsenious and Arsenic Acids.**

GEORG JOACHIMOGLU (*Arch. Exp. Path. Pharm.*, 1916, **80**, 8—24).—The author shows that, on adding sodium arsenite to weakly alkaline urine and extracting it with alcohol, arsenic can be established both in the alcohol and in the residue. He therefore maintains that Salkowski is not justified in concluding that the arsenic found in an alcoholic extract of urine is of an organic nature. The author further criticises the various methods employed for the estimation of arsenic acid in the presence of arsenious acid, and considers that results obtained by such methods are not valid. He shows, on the other hand, that by means of electrolysis in alkaline solution, arsenious acid can be established with certainty in the presence of arsenic acid. Employing this method, he demonstrates that by injecting subcutaneously arsenic acid in dogs, at least 16% of the arsenic is excreted in the urine as arsenious acid.  
S. S. Z.

**The Nature of Excreted Arsenious and Arsenic Acids.**

E. SALKOWSKI (*Arch. Exp. Path. Pharm.*, 1916, **80**, 231—235, 319—320); G. JOACHIMOGLU (*ibid.*, 317—318).—Polemical in reference to Joachimoglu's criticisms (see preceding abstract) on Salkowski's earlier work.  
S. S. Z.

**Influence of Adsorbent (especially Colloidal) Substances on the Separation of Uric Acid and its Salts from Supersaturated Solution.** RUDOLF KOHLER (*Z. klin. Med.*, 1919, **88**, 14; *Zentr. Biochem. Biophys.*, **21**, 354—355).—In connexion with the work of Marc and with reference to the observations of Lichtwitz, the author has studied the influence of colloidal and other adsorbent substances on the separation of urates from supersaturated solutions. The conclusions deduced by Marc are essentially applicable to uric acid, but the retarding action is relatively small. This action applies only to the beginning of the separation and varies in a parallel manner with the adsorbability; its magnitude depends on the amount of substance which is added and the reciprocal value of the degree of supersaturation. The insignificance of this effect is explained by the fact that uric acid in solution (also its salts) has such a pronounced tendency towards supersaturation that the influence of the colloid has little relative value. Contrary to the view of Lichtwitz, the author does not, therefore, attach much importance to the action of colloids in holding crystalloids in solution in the urine and other fluids of animal origin. Colloids are superfluous, or at least of secondary importance, in so far as an explanation of the great solubility of uric acid in fluids of animal origin is concerned.  
CHEMICAL ABSTRACTS.

**The Elimination of Taurine Administered to Man.**

CARL L. A. SCHMIDT and E. G. ALLEN (*J. Biol. Chem.*, 1920, **42**, 55—58).—Estimations of neutral sulphur and amino-acid nitrogen in the urine of an individual to whom had been given 10 grams of taurine per os show a close agreement, which indicates



that taurine is not eliminated as taurocarbamic acid (Salkowski, this Journ., 1872, 1033; 1874, 1129). Administration of taurine in large doses does not result in any marked changes in the excretion of urea and ammonia.

J. C. D.

**Excretion of Quinine in the Urine.** M. NIERENSTEIN (Extract from Observations on Malaria, War Office, 1919, pp. 1—79).—See this vol., ii, 456.

**Presence of True Mucin in Certain Urines.** CH. O. GUILLAUMIN (*J. Pharm. Chim.*, 1920, [vii], 21, 337—342).—The author has detected the presence of mucin in two samples of urine, both of which were distinctly acid in reaction.

W. P. S.

**Urochrome.** J. MELLANBY and C. J. THOMAS (*Proc. Physiol. Soc.*, 1920; *J. Physiol.*, 1920, 53, xcvi).—The pigment of urine is readily absorbed by animal charcoal of good quality. After washing the charcoal with warm water to remove traces of other urinary constituents, the pigment is removed with 50% alcohol containing 0.5% sodium hydroxide. After neutralisation with sulphuric acid, the fluid is concentrated, and the greater part of the sodium sulphate removed by crystallisation. From the aqueous solution, the pigment is precipitated by alcohol, washed with ether, and dried in a vacuum. The pigment may be purified further by repeated reprecipitation. It is a brown, amorphous powder, very soluble in water, but insoluble in the usual organic solvents. It shows no characteristic absorption bands. The aqueous solution slowly dialyses through parchment. No definite evidence of its metabolic significance has yet been obtained, but its excretion is roughly parallel with that of creatinine.

J. C. D.

**Physiological Radioactivity.** H. ZWAARDEMAKER (*J. Physiol.*, 1920, 53, 273—289. Compare A., 1917, i, 241).—In a large number of systems, the potassium ion may, as regards function, be replaced by all the other radioactive elements, the heavy ones as well as the light ones, provided the doses are equiradioactive.

When applied simultaneously, the substances emitting  $\alpha$ -rays and those emitting  $\beta$ -rays are reciprocally antagonistic.

Potassium is (as a bearer of physiological radioactivity) for many cells a stimulus, which can restore and sustain function when it is brought in contact with the surface of the cells as a free, diffusible ion in the circulating fluid. A free radioactive radiation can take the place of potassium when previously the potassium is omitted from the circulation.

J. C. D.

**The Theory of Narcosis.** E. VON KNAFFL-LENZ (*Arch. Exp. Path. Pharm.*, 1919, 84, 66—88).—The surface tension against air and paraffin, and the partition coefficient in oil and water of the aqueous solution of various narcotics were determined at 10°, 20°, and 30°. The alterations in the surface tension, both against air and paraffin, at the different temperatures were not proportional

to the narcotic potency. A better agreement could be established between the partition coefficient and the narcotic potency, and the author therefore maintains that Traube's objections to the lipid theory of narcosis are not justified. The influence of the vapour of volatile narcotics on jellies was also studied, and it was found, in contradistinction to Traube's results, that not only do the vapours not promote imbibition, but they produce the opposite effect. S. S. Z.

**Relation between Chemical Constitution and Physiological Action in Local Anæsthetics. I. Homologues of Procaine.** OLIVER KAMM (*J. Amer. Chem. Soc.*, 1920, **42**, 1030—1033).—See this vol., i, 482.

**Carbon Monoxide in Tobacco Smoke.** H. HARTRIDGE (*Proc. Physiol. Soc.*, 1920; *J. Physiol.*, 1920, **53**, lxxxii).—The positive results indicate the possibility of there being in a heavy smoker a condition of chronic carbon monoxide poisoning.

J. C. D.

**Toxicity of Some Inorganic Substances to Paramœcium.** N. McCLELAND and R. A. PETERS (*Proc. Physiol. Soc.*, 1919; *J. Physiol.*, 1919, **53**, xii).—There is a slight suggestion of a periodic rise and fall in toxicity with increase in molecular weight; thus vanadium-manganese-iron-nickel-cobalt-calcium, also silver-cadmium-tin-mercury-thallium(ic)-lead, seem to form such a series. The most toxic metals are bivalent. J. C. D.

**Chemical Constitution and Physiological Action. The Toxicity of some Organic Metal Derivatives and some other Organic Substances.** N. McCLELAND and R. A. PETERS (*J. Physiol.*, 1919, **53**, xv).—The relation of chemical constitution to physiological action was tested by toxicity tests on *Paramoecia*. These preliminary experiments indicate that primary compounds are less toxic than secondary, that aliphatic compounds are less toxic than aromatic, and that arsenic compounds are less toxic than those of antimony. J. C. D.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Fermentation Characteristics of certain Pentose-destroying Bacteria.** E. B. FRED, W. H. PETERSON, and AUDREY DAVENPORT (*J. Biol. Chem.*, 1920, **42**, 175—189).—The average limit of growth in the yeast-water medium was approximately  $p_H$  3.6 to 4.0 in the case of xylose, dextrose, galactose, sucrose, lævulose, and lactose. Mannitol was decomposed more slowly, and

gave a limit of about  $p_H$  4.3. Acidity measurements and observation of the volume of gas liberated give no idea of the amount of carbohydrate fermented. The pentose sugars, arabinose and xylose, form on fermentation more than 20% of normal acid, divided into almost equal amounts of lactic acid and acetic acid. Rhamnose is not attacked by these organisms. The aldo-hexoses, dextrose and galactose, yield acetic acid, lactic acid, and ethyl alcohol, but the acid formation is small as compared with that observed in the fermentation of the pentose sugars. Mannose ferments more slowly than either dextrose or galactose, and yields nearly equal quantities of volatile and non-volatile acids. The ketone sugar, lævulose, is rapidly reduced by the pentose-fermenting organisms to form mannitol, volatile and non-volatile acids and carbon dioxide being formed at the same time. The chief disaccharides are all fermented, but never completely. Raffinose and melizitose are not attacked. A number of other substances were examined. Mannitol, glycerol, salicin, and xylan are slowly decomposed; æsculin, starch, inulin, cellulose, succinic, tartaric, and citric acids are not attacked, whilst pyruvic, lactic, and malic acids ferment, giving rise to closely related acids.

J. C. D.

#### Sensitiveness of Yeast Fermentation to the $P_H$ Value.

H. VON EULER and S. HEINTZE (*Arkiv. Kem. Min. Geol.*, 1917, 7, No. 21, 1—21).—The fermentation of sucrose and dextrose by yeast has been investigated at 28° in the presence of hydrochloric acid of varying concentrations with the object of ascertaining the dependence of the rate of fermentation on the  $P_H$  value of the solution. The  $P_H$  value was determined by Sørensen's indicator method, and the velocity of fermentation by direct measurement of the volume of carbon dioxide evolved in a given time by 200 yeast cells. All experiments were carried out at 28°. The maximum velocity of fermentation lies at  $P_H=5$ , and this is also found when yeast-water or asparagine is added to the fermentation mixture, although in these cases the velocity is very much greater than in solutions which contain no absorbable nitrogen compound. The relative maximum velocities, expressed in c.c. of carbon dioxide evolved per hour, are: solutions without added nitrogen compounds, 75 c.c.; solutions with asparagine, 134 c.c.; solutions with yeast-water, 187 c.c. Oxalic acid and chromic acid in concentrations up to 0.025*N* do not act as yeast poisons, as has been frequently stated. In solutions of hydrochloric acid up to 0.01*N*, the influence of the chlorine ions is unimportant, as also is the influence of the non-ionised molecules, but with weak organic acids the undissociated molecules play a considerable part.

J. F. S.

#### Nitrogen of the Cyanogen Group in Fertilisation. R.

PEROTTI (*Atti R. Accad. Lincei*, 1920, [v], 29, i, 206—210).—In presence of suitable nutrient substances, such as dextrose, potassium cyanide in concentrations of the order of 0.05% serves as nitrogenous nutriment for micro-organisms of various kinds.

T. H. P.

**The Properties of Colloidal Systems. IV. Reversible Gelation in Living Protoplasm.** W. M. BAYLISS (*Proc. Roy. Soc.*, 1920, [B], **91**, 196—201).—By means of suitable optical arrangements giving an intense dark-ground illumination, it is possible to see that the apparently clear pseudopodia of *Amoeba* are filled with numerous very minute particles in Brownian movement. This affords further evidence of the hydrosol nature of simple protoplasm. By suitable electrical stimulation, this sol can be reversibly changed into the gel state, the change being shown by the sudden cessation of the Brownian movement, which recommences when the stimulation is stopped. W. G.

**Formation of Starch in Green Plants.** C. RAVENNA (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 148—150).—Polemical. T. H. P.

**Hydration Effects of Amino-compounds.** D. T. MACDOUGAL and H. A. SPOEHR (*Proc. Soc. Expt. Biol. Med.*, 1919, **17**, 33—36; from *Physiol. Abstr.*, 1920, **5**, 102).—Experiments made on the swelling of agar and plant gums in solutions of amino-acids, both in the presence and absence of proteins, show that when the amino-acid is one which dissociates strongly, the swelling is less than in water. The reverse also holds. The concentration of hydrogen ions is not the only factor. J. C. D.

**Distribution of certain Chemical Constants of Wood over its Proximate Constituents.** W. H. DORE (*J. Ind. Eng. Chem.*, 1920, **12**, 472—476).—About one-half of the furfuraldehyde-yielding groups in redwood (*Sequoia sempervirens*) is associated with the cellulose, and only a small amount with the lignin. The acetic acid-yielding groups are associated with the cellulose and to a small extent with the lignin, whilst the methoxy-groups are associated entirely with the lignin. W. P. S.

***Caltha palustris*.** E. POULSSON (*Arch. Exp. Path. Pharm.*, 1916, **80**, 173—183).—The chemical nature of the active principle of *Caltha palustris* (marsh marigold) was investigated. On distilling the aqueous extract of the fresh plant with sodium carbonate in steam, only ammonia was obtained. The author then had recourse to the potassium bismuth iodide method of precipitation employed by Jahns. The only base obtained in this way was choline. By precipitating the extract with phosphotungstic acid and examining the various fractions again, only choline was established. The author concludes that the traces of alkaloids and alkaloidal substances previously observed in extracts of *Caltha palustris* were choline. S. S. Z.

**Fat-soluble Vitamine. VI. The Extractability of the Fat-soluble Vitamine from Carrots, Lucerne, and Yellow Corn by Fat Solvents.** H. STEENBOCK and P. W. BOUTWELL [with MARIANA T. SELL and E. G. GROSS] (*J. Biol. Chem.*, 1920, **42**, 131—152).—Fat solvents, such as ether, chloroform, and

carbon disulphide, remove little or none of the fat-soluble accessory factor from carrots; alcohol and benzene, however, remove considerable amounts. Ether, benzene, and alcohol all removed a considerable proportion of the vitamine from lucerne. The superiority of alcohol as an extracting fluid is also demonstrated in the examination of yellow maize. The vitamine extracted from lucerne with alcohol resists hydrolysis with alcoholic potassium hydroxide in the cold, and can be recovered in the carrotene fraction of the unsaponifiable matter. The xanthophyll fraction is practically inactive.

J. C. D.

**Occurrence and Reactions of Anthocyanin Colouring Matters of the Beet-red Group.** FERDINAND KRYZ (*Oesterr. Chem. Zeit.*, 1920, **23**, 55—56).—Members of the beet-red group of anthocyanins (Weigert, A., 1896, i, 387; Hilger and Mai, *ibid.*, 496) occur in the skins of fuchsia and cacti berries, and in the petals of scarlet cactus blooms. Fuchsia anthocyanin is insoluble in ether, chloroform, carbon disulphide, and amyl alcohol, but gives a carmine solution in acidified acetone or amyl alcohol. Potassium hydroxide or ammonia produces the characteristic yellow coloration, which becomes reddish with excess; organic acids or concentrated hydrochloric or sulphuric acid, a blackberry-red coloration, not destroyed by heat; nitric acid, a red coloration, yellow on warming; sodium carbonate, a dirty reddish-yellow coloration, bright yellow on warming; sodium hydrogen carbonate, a blue coloration, green on warming; mercuric chloride, sodium hydrogen sulphite, or bleaching powder, a light yellow coloration. Cactus bloom anthocyanin is soluble in water, methyl, ethyl, and acidified amyl alcohols, and in glycerol, but insoluble in ether, chloroform, and carbon disulphide. The details given in regard to the effect of reagents on it are very similar, except that the last-mentioned reagents cause decolorisation, slowly at the ordinary temperature, immediately on warming. The colouring matter from red beet also gives these reactions, and is soluble in cold acetone. Wing cactus blooms apparently contain two anthocyanins, because the reddish-yellow extract obtained with hot acetone exhibits slight differences from the above products, whilst the red aqueous solution of the residue gives all the above reactions.

J. K.

**Proteins from the Georgia Velvet Bean, *Stizolobium Deeringianum*.** CARL O. JOHNS and HENRY C. WATERMAN (*J. Biol. Chem.*, 1920, **42**, 59—69).—The Georgia velvet bean contains 23·6% of protein ( $N \times 6\cdot25$ ). About 15% of protein is extracted by a 3% aqueous sodium chloride. By fractional precipitation with ammonium sulphate, and by subsequent purification of the fractions, two globulins, designated  $\alpha$  and  $\beta$ , may be separated, in yields of about 3 and 1·25% respectively. An albumin may also be isolated in yields of about 0·75%. When analysed by Van Slyke's method, the three proteins show marked differences. There is apparently no tryptophan in the  $\beta$ -globulin.

J. C. D.

**Exosmosis of Acid Principles and Sugars from the Orange.** G. ANDRÉ (*Compt. rend.*, 1920, **170**, 1199—1201).—During exosmosis, the ratio of the citric acid to the total sugars, reducing and non-reducing, which have diffused out remains constant. Similarly, the ratio of sucrose to reducing sugars is fairly constant, but in considering this ratio it must be remembered that inversion of a portion of the sucrose occurs during exosmosis.

W. G.

**The Proteins of Green Leaves. I. Spinach Leaves.** THOMAS B. OSBORNE and ALFRED J. WAKEMAN [with CHARLES S. LEAVENWORTH and OWEN L. NOLAN] (*J. Biol. Chem.*, 1920, **42**, 1—26).—By diluting the thoroughly ground leaves with one or two volumes of water and centrifugalising the extract at high speed, a solution of leaf proteins may be obtained. From this, impure protein substances may be precipitated by the addition of alcohol. This fraction is considerably purified from pigments and other substances by extraction with alcohol and ester, yielding a nearly colourless product containing about 14% of nitrogen, calculated on the ash free substance. At least 40% of the total nitrogen of spinach leaves is contained in colloidal protein; about one-third in substances which are soluble in water; and a comparatively small part in chlorophyll, phosphatides, and, presumably, nucleic acid. There are reasons for believing that certain of the constituents of the cell exist normally in the form of complexes. Examination of spinach leaves dried by warm air below 60° showed that their composition closely resembles that of the fresh leaves.

It is possible that the protein of the spinach leaves is in some form of combination with a substance of a pentosan nature, but confirmation of this has not yet been obtained. J. C. D.

**Action of Hydrogen Cyanide on the Organism of Plants.** JULES STOKLASA (*Compt. rend.*, 1920, **170**, 1404—1407).—Micro-organisms offer a considerable resistance to hydrogen cyanide. Exposure to an atmosphere containing 2% by volume of this gas for twenty-four hours at 13—14° only slackened the development without stopping it in the case of *B. subtilis* and *B. mesentericus vulgatus* and certain phycomycetes. *Tilletia tritici* was, however, completely destroyed by exposure to such a concentration for twenty-four hours at 16°. Such an exposure in no way injured the germination of wheat, barley, or beetroot seeds, provided the seeds were freely exposed to the air for three days and stirred frequently before germination.

W. G.

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which would consequently be far less reactive than the simpler molecule. This accords well with the experimentally established fact that such polymerides are in general much less active than the simple substances, with which, however, they usually have certain actions in common.

H. W.

**Partial Condensation of Natural Gas at Liquid Air Temperatures and a Curious Effect Observed with the Nitrogen which Dissolves in the Condensate.** JOHN SATTERLY (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 109—121).—Methods for the preliminary separation of natural gas by condensation are described. Sudden solution and expulsion of nitrogen by liquid methane occurred. [See *J. Soc. Chem. Ind.*, 1920, 539A.]

J. R. P.

**The Oxidation of Paraffins.** AD. GRÜN [with E. ULBRICH and TH. WIRTH] (*Ber.*, 1920, **53**, [B], 987—996).—The recent publication of Kelber (this vol., i, 280) has induced the author to place on record some of the results obtained by himself.

Under suitable conditions, pure paraffins, or mixtures such as vaselin or petroleum, are readily oxidised to fatty acids by air or even by gaseous mixtures containing as little as 1% of oxygen. The statements by various authors that the process can be catalytically accelerated by suitable oxygen carriers are, in general, erroneous, and depend, in part at any rate, on insufficiently extended analyses of the products. Thus a series of experiments carried out with a paraffin, m. p. 52°, at 160° showed that metallic oxides, such as lime and barium oxide, salts with an alkaline reaction, and certain neutral substances, such as carbon and fuller's earth, are particularly harmful, whilst acidic substances, such as stearic acid, are, according to the properties of the hydrocarbon used, either helpful or at any rate not markedly inhibitive. If the conditions of reaction are not carefully chosen, one carbon atom after another of the intermediate products can be oxidised away, and the whole series of acids from those of high molecular weight to the volatile acids, and ultimately to formic acid or carbon dioxide, may be obtained. Particularly when oxygen is used, the action is likely to lead to violent explosions, due to the intermediate formation of peroxides.

The products of oxidation differ not only quantitatively, but also qualitatively, according to the conditions of experiment. The most interesting observation is that, when the conditions are not too vigorous, the product consists of mixtures of waxes with more or less free acid, alcohols, and some unsaponifiable matter. The composition of the mixture of acids depends entirely on factors, such as temperature, duration of action, etc., and may consist mainly of the series  $C_{16}$  to  $C_{22}$  or higher, or of such in which  $C_{10}$  to  $C_{14}$  or  $C_{15}$  predominate. Hydroxy-fatty acids are also formed, and are present partly in the form of esters or estolides, whilst unsaturated acids, probably derived from the hydroxy-acids by loss of water, are also found. The unsaponifiable matter consists

to a small extent of unchanged paraffin, but chiefly of higher alcohols with some carbonyl compounds. The separation of these products is a matter of difficulty, since the usual qualitative and quantitative carbonyl reactions are not trustworthy with substances of high molecular weight. Removal of the carbonyl derivatives is most readily effected indirectly by reducing them to alcohols by sodium and amyl alcohol, and their amount can be indirectly estimated by determining the hydroxyl number of the product before and after such treatment. They appear to consist of a mixture of aldehydes with certain amounts of ketones.

The results so far obtained do not permit any definite conclusion to be drawn with regard to the course of the oxidation; it would appear, however, that molecular oxygen attacks the carbon chain at a greater distance from the methyl group than is to be expected from analogous processes.

H. W.

### Fatty Acids Obtained by the Oxidation of Paraffins.

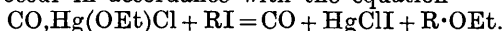
FRANZ FISCHER and WILHELM SCHNEIDER (*Ber.*, 1920, **53**, [B], 922—925).—Pure paraffin or crude expressed paraffin is heated with dilute sodium carbonate solution in a steel autoclave at about 170°, whilst simultaneously compressed air is pumped through the mixture. The paraffins are considerably more rapidly oxidised under these conditions than at atmospheric pressure, and the yield of fatty acids is as high as 90% of the paraffin used. The rate of reaction depends on the temperature in the usual manner, and is proportional to the pressure of the air. Iron, manganese, and copper have approximately equal catalytic effects, but the other substances investigated are less active, possibly in part owing to the catalytic activity of the steel walls of the autoclave. Under the same conditions, the quantity of fatty acids produced per hour is, within limits, proportional to the amount of paraffin, but the highest yields per given time are best obtained by working so as to secure complete neutralisation of the sodium carbonate solution rather than complete utilisation of the paraffin. Examination of the fatty acids, which are purified in the usual manner, shows that they are true, monobasic fatty acids, the density of which is less than unity, and that they dissolve completely in light petroleum; unlike the more common members, however, they contain an uneven number of carbon atoms. The following have been definitely characterised:  $C_{19}H_{38}O_2$ , m. p. 65—66°;  $C_{17}H_{34}O_2$ , m. p. 58—59°;  $C_{15}H_{30}O_2$ , m. p. 50—51°;  $C_{13}H_{26}O_2$ , m. p. 38°.

Re-examination of a patented process for the oxidation of paraffin by blowing air through the substance heated at 135—145° in an iron vessel in the absence of water shows that the actual products are the acid anhydrides, which can be separated from unaltered paraffin by taking advantage of the insolubility of the latter in acetone.

H. W.

**The Constitution of the Mercury Compounds of Carbon Monoxide and of Ethylene.** WILHELM MANCHOT (*Ber.*, 1920, **53**, [B], 984—987).—The author's experiments (the full details

of which will be published elsewhere) lead him to the conclusion that the ethylene compounds mentioned in the title are to be regarded as additive products of ethylene and basic mercury salt,  $C_2H_4.Hg(OH)X$ , and not as structural compounds, as formulated by Schoeller, Schrauth, and Essers (A., 1913, i, 1162; this vol., i, 225). The close similarity between these substances and those given by carbon monoxide indicates a similar structure for the latter also. This conclusion is supported by the fact that methyl acetatomercuriformate yields carbon monoxide, mercury iodide, and mercury acetate when heated with methyl iodide at  $100^\circ$ , whereas, according to the structural formulation, mercuric iodide and methyl acetate would be expected; similarly, ethyl chloromercuriformate and *n*-propyl iodide yield carbon monoxide and mercury haloid without a trace of methyl butyrate. Reaction appears to occur in accordance with the equation



The mercury derivatives obtained by Schoeller and Schrauth by the action of ethylene on an alcoholic solution of mercury acetate behave similarly to those prepared in aqueous solution and also to the carbon monoxide compounds; in particular, they are extremely readily decomposed by halogen acids, with liberation of ethylene, whilst the latter is also evolved when they are treated with alkyl iodides. Their constitution may therefore be expressed by the formula  $C_2H_4.Hg(OEt)X$ . H. W.

**Preparation of Dimethylbutadiene.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 319505; from *Chem. Zentr.*, 1920, ii, 776).—Pinacone chlorohydrin is treated with hydroxyl-free substances which can combine with acids, such as ammonia or organic bases. Thus, when it is distilled with dimethylaniline, a mixture of water and dimethylbutadiene passes over between  $60^\circ$  and  $80^\circ$ . H. W.

**Production of True Acetylenic Hydrocarbons from *epi*-Dibromhydrin.** R. LESPIEAU and BOURGUEL (*Compt. rend.*, 1920, 170, 1584—1586).—*epi*-Dibromohydrin,  $CH_2Br.CBr:CHBr$ , reacts in the cold with mixed magnesium derivatives to give compounds of the type  $CH_2:CBr.CH_2R$ , which, when acted on by alcoholic potassium hydroxide, lose the elements of hydrogen bromide, giving an acetylenic hydrocarbon, but the action is complicated by the tendency of the triple linking to migrate. A better method is to prepare a tribromide from the compound,  $CH_2:CBr.CH_2R$ , and then act on this with sodium ethoxide, the product being  $CHBr:CBr.CH_2R$ , which, when acted on by zinc in alcoholic solution, gives the required acetylenic hydrocarbon,  $CH:C.CH_2R$ . Thus *epi*-dibromohydrin condenses with magnesium ethyl bromide to give  $\beta$ -bromopentene, b. p.  $107$ — $108^\circ$ ,  $D_4^{20}$  1.277. This compound unites with bromine to give  $\alpha\beta\beta$ -tribromopentane, b. p.  $108$ — $109^\circ$ /17 mm.,  $D_4^{20}$  2.03, which with sodium ethoxide yields  $\alpha\beta$ -dibromopentene, b. p.  $66$ — $67^\circ$ /19 mm.,  $D_4^{20}$  1.73. This compound, when

treated in alcoholic solution with zinc, gives  $\Delta^{\alpha}$ -pentinene,  
 $\text{CH}:\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$ .  
 W. G.

**Production of Chloropicrin.** KENNEDY JOSEPH PREVITÉ ORTON and (SIR) WILLIAM JACKSON POPE (Brit. Pat. 142878).—Chloropicrin is obtained by the action of chlorine in presence of water on picric acid or other suitable nitrophenol, a sufficient amount of alkali, preferably sodium hydroxide or carbonate, being added either before or during the reaction to dissolve the nitro-compound and neutralise the acid produced according to the equation  $\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OH} + 11\text{Cl}_2 + 5\text{H}_2\text{O} = 3\text{CCl}_3\cdot\text{NO}_2 + 13\text{HCl} + 3\text{CO}_2$ . For example, 1 part of picric acid may be dissolved in a solution of 2.975 parts of sodium hydroxide in 50 parts of water, and, after cooling to 2–4°, whereby sodium picrate separates in small crystals, a slow, intermittent stream of chlorine is led in until the colour of the solution is discharged. The chloropicrin separates as an almost colourless oil, and amounts to 180–190% of the weight of picric acid taken.  
 G. F. M.

**The Effect of Reducing Agents on Tetranitromethane, and a Rapid Method of Estimation.** AILEEN BAILLIE, ALEXANDER KILLEN MACBETH, and NORAH IRENE MAXWELL (T., 1920, 117, 880–884).

**Corrections for Densities of Ethyl Alcohol to 15.5°/15.5°.** H. DROOP RICHMOND (*Analyst*, 1920, 45, 222).—A table is given showing the corrections to be made when the specific gravity is determined at temperatures between 10° and 25°, and for a range in specific gravity from 0.79 to 0.99.  
 W. P. S.

**Preparation of Polyhydroxy-alcohols.** OSCAR MATTER (D.R.-P. 299074; from *Chem. Zentr.*, 1920, iv, 14).—The requisite halogenated hydrocarbons are hydrolysed by aqueous solutions of carbonates or hydrogen carbonates, or mixtures thereof; as the reaction proceeds, the used hydrolysing agent is regenerated by addition of alkali hydroxide solution. Addition may be made periodically or continuously, at will or automatically. When using closed vessels, the concentration of the reagent may be maintained uniform during the whole experiment. The rate of reaction is thereby increased during the whole time, but particularly towards the end; concentrated products are obtained and the pressure in the vessel is lessened. The preparation of ethylene glycol from ethylene chloride and sodium carbonate or hydrogen carbonate at 130–140° is cited. .  
 H. W.

**A Hydrate of an Oxonium Compound.** O. MAASS and J. RUSSELL (*Trans. Roy. Soc. Canada*, 1919, 13, iii, 259–264).—A termolecular compound of ethyl ether, hydrogen bromide, and water was isolated by the freezing-point curves of the system  $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{HBr}$  and  $\text{H}_2\text{O}$ . The formula of the compound was found to be  $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{HBr}\cdot\text{H}_2\text{O}$ . The catalytic effect of mineral

acids in esterification is attributed to their linking the alcohol and organic acid in a molecular complex, where opportunity is afforded for interchange of radicles. A definite compound of ethyl alcohol and ethyl ether-hydrobromide could not be obtained. J. R. P.

**Preparation of Ethylene Oxide.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 299682; from *Chem. Zentr.*, 1920, iv, 16).—(i) Bases are added to warm ethylene chlorohydrin or its solutions. (ii) When bases other than alkalis are used, the order of addition of the substances may be changed. Excellent yields of ethylene oxide are obtained, whereas ethylene glycol and polyethylene glycols are mainly produced when the chlorohydrin is added to the warm alkali solution. H. W.

**The Xanthates of Cobalt and Nickel.** MARCEL DELÉPINE and LOUIS COMPIN (*Bull. Soc. chim.*, 1920, [iv], 27, 469—474. Compare this vol., i, 536, and Dubskey, A., 1914, ii, 732).—These xanthates were prepared by double decomposition with alkali xanthates. The nickel salts crystallise much more readily than the cobaltic salts, the former being also more stable than the latter. As with the dithiocarbamates, there is a tendency to get some cobaltous salt along with the cobaltic salt, the tendency increasing with the molecular weight. The nickel salts are black, the cobaltic salts deep green or black, and the cobaltous salts brown. The salts described are *cobaltic methylxanthate*; *cobaltic* and *nickel ethylxanthates* (compare Dubskey, *loc. cit.*); *cobaltic* and *nickel n-propylxanthates*, *cobaltic* and *nickel n-butylxanthates* and *isobutylxanthates*; *cobaltic*, *cobaltous*, and *nickel isoamylxanthates*; *cobaltic* and *cobaltous benzylxanthates*; *cobaltic isopropylxanthate*; *cobaltic* and *nickel sec-butylxanthates*; *cobaltic* and *cobaltous menthylxanthates*. W. G.

**Trimethylsulphonium Compounds.** HILDEGARD BLÄTTLER (*Monatsh.*, 1919, 40, 417—429).—The author has prepared a number of double compounds formed from trimethylsulphine chloride, bromide, and iodide with a number of metallic salts. Methods are given for the preparation of methyl hydrogen sulphate and methyl sulphide.

Unlike methyl iodide, methyl chloride combines with difficulty with methyl sulphide, this combination not being aided materially by addition of zinc chloride or cadmium chloride, although the formation of double sulphinium compounds from metallic salt, sulphide, and alkyl haloid often proceeds considerably more readily than the union of sulphide and alkyl haloid alone. For the preparation of the other double chlorides, use was made, therefore, of trimethylsulphine chloride previously obtained.

Trimethylsulphine chloride is best obtained by treating an aqueous solution of the corresponding iodide with silver chloride; it decomposes at 100°, and has m. p. 100—117°.

*Bistrimethylsulphine cupric chloride*,  $(\text{SMe}_3)_2\text{CuCl}_4$ , forms orange-yellow crystals, which soften and turn black at 180° and melt com-

pletely at  $190^{\circ}$ . *Bistrimethylsulphine zinc chloride*,  $(\text{SMe}_3)_2\text{ZnCl}_4$ , white, non-hygroscopic crystals, m. p.  $208^{\circ}$ . *Trimethylsulphine cadmium chloride*,  $\text{SMe}_3\text{CdCl}_3$ , white, non-hygroscopic needles or fan-like aggregates, subliming slightly, but not melting, at  $430^{\circ}$ . *Bistrimethylsulphine manganous chloride*,  $(\text{SMe}_3)_2\text{MnCl}_4$ , pale yellow, non-hygroscopic crystals, remaining unchanged at  $300^{\circ}$ . *Trimethylsulphine ferrous chloride*,  $\text{SMe}_3\text{FeCl}_3$ , m. p. (impure?)  $190^{\circ}$ . *Trimethylsulphine ferric chloride*,  $\text{SMe}_3\text{FeCl}_4$ , pale yellowish-brown crystals, softening at  $240^{\circ}$ , m. p.  $250^{\circ}$ . *Trimethylsulphine bismuth chloride* (?),  $\text{SMe}_3\text{BiCl}_4$  (?), white, crystalline precipitate. *Trimethylsulphine stannic chloride*,  $\text{SMe}_3\text{SnCl}_5$ , white precipitate, unmelted at  $300^{\circ}$ .

Trimethylsulphine bromide (compare Cahours, this Journ., 1875, 1181; 1876, i, 696; Carrara, A., 1892, 1422), readily obtained from the iodide and silver bromide, forms colourless, transparent, deliquescent plates, and begins to melt at  $184^{\circ}$  and volatilises completely at  $189^{\circ}$ . With copper bromide in methyl-alcoholic solution, it gives a deep violet precipitate, m. p.  $184$ — $185^{\circ}$ . *Bistrimethylsulphine zinc bromide*,  $(\text{SMe}_3)_2\text{ZnBr}_4$ , forms white, non-hygroscopic crystals, m. p.  $211$ — $213^{\circ}$ . *Trimethylsulphine cadmium bromide*,  $\text{SMe}_3\text{CdBr}_3$ , white, non-hygroscopic crystals, sinters at about  $180^{\circ}$ , m. p. (frothing)  $233$ — $235^{\circ}$ . *Bistrimethylsulphine bismuth bromide*,  $(\text{SMe}_3)_2\text{BiBr}_5$ , pale yellow precipitate, swells at about  $220^{\circ}$ , m. p.  $223^{\circ}$ .

Trimethylsulphine iodide has m. p.  $184$ — $185^{\circ}$  (compare Klinger, A., 1878, 128; Strömholm, A., 1900, i, 325). *Bistrimethylsulphine zinc iodide*,  $(\text{SMe}_3)_2\text{ZnI}_4$ , forms white, non-hygroscopic crystals, m. p.  $183^{\circ}$ . *Trimethylsulphine bismuth iodide*,  $\text{SMe}_3\text{BiI}_4$ , red salt, not melting at  $290^{\circ}$  (compare Vanino and Mussnug, A., 1917, i, 196).

T. H. P.

**Preparation of  $\beta\beta'$ -Dichloroethyl Sulphide.** (SIR) WILLIAM JACKSON POPE, CHARLES STANLEY GIBSON, and HENRY FLEETWOOD THUILLIER (Brit. Pat. 142875).— $\beta\beta'$ -Dichloroethyl sulphide is obtained in upwards of 90% yield by passing dry ethylene into sulphur monochloride heated to, and maintained at,  $50$ — $70^{\circ}$ , until no further absorption occurs. The reaction is facilitated by introducing a small proportion of dichloroethyl sulphide into the sulphur monochloride before treatment with ethylene. The product is conveniently separated from the sulphur simultaneously formed by heating the reaction mixture to  $100^{\circ}$  and allowing to cool, when the sulphur is deposited in crystalline form and the supernatant liquid can be poured off.

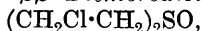
G. F. M.

**$\beta\beta'$ -Dichlorodiethyl Sulphide and certain of its Derivatives.** WILHELM STEINKOPF, JULIUS HEROLD and JOSEPH STOHR (Ber., 1920, 53, [B], 1007—1012).— $\beta\beta'$ -Dichlorodiethyl sulphide,  $\text{S}(\text{CH}_2\cdot\text{CH}_2\text{Cl})_2$ , is readily prepared as a colourless oil, b. p.  $108$ — $109^{\circ}/15$  mm. (yield, 83%), by the action of thionyl chloride on  $\beta\beta'$ -dihydroxydiethyl sulphide in the presence of chloroform. It is oxidised by hydrogen peroxide to the corresponding

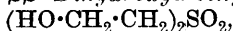
*sulphoxide*, m. p.  $109^{\circ}$ , and by potassium permanganate to the *sulphone*, colourless crystals, m. p.  $48^{\circ}$ , b. p.  $179\text{--}181^{\circ}/14\text{--}15$  mm.  $\beta$ -Hydroxydiethyl sulphide,  $\text{SEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , b. p.  $182\text{--}184^{\circ}$ , is conveniently obtained by the addition of ethylene chlorohydrin to ethyl mercaptan dissolved in a solution of sodium in alcohol. It is converted by phosphorus tribromide into  $\beta$ -bromodiethyl sulphide, b. p.  $83\text{--}86^{\circ}/29$  mm.  $\beta\beta'$ -Dibromodiethyl sulphide, from  $\beta\beta'$ -dihydroxydiethyl sulphide and phosphorus tribromide, has b. p.  $115.5^{\circ}/1$  mm., m. p.  $31\text{--}34^{\circ}$ .  $\beta\beta'$ -Dithiocyanodiethyl sulphide is prepared by heating the corresponding chloride with sodium thiocyanate in acetone solution; it forms bright yellow crystals, m. p.  $35^{\circ}$ .  $\beta\beta'$ -Dicyanodiethyl sulphide could not be prepared, but  $\beta\beta'$ -dicyanodimethyl sulphide, m. p.  $47.5^{\circ}$ , b. p.  $177\text{--}178^{\circ}/22$  mm., was obtained by the action of potassium sulphide on chloroacetonitrile. Phenyl  $\beta$ -chloroethyl sulphide,  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{SPh}$ , b. p.  $144.5^{\circ}/26$  mm.,  $245^{\circ}/\text{atmospheric pressure}$ , was prepared from ethylene chlorohydrin and thiophenol in the presence of a solution of sodium in ethyl alcohol. H. W.

### Reactions and Derivatives of $\beta\beta'$ -Dichlorodiethyl Sulphide.

OREGON B. HELFRICH and E. EMMET REID (*J. Amer. Chem. Soc.*, 1920, **42**, 1208—1232).— $\beta\beta'$ -Dichlorodiethyl sulphoxide,



plates, m. p.  $109.5^{\circ}$ , is obtained by diluting a solution prepared by the addition of  $\beta\beta'$ -dichlorodiethyl sulphide to concentrated nitric acid at the ordinary temperature. On distillation, even under reduced pressure, it is partly decomposed into the sulphide, but it is unchanged by boiling water or silver nitrate solution; alcoholic sodium hydroxide converts it into dihydroxydiethyl sulphoxide,  $(\text{HO}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}$ , a viscous, oily liquid, easily soluble in water. The dichloro-compound apparently has no action on the skin, whereas dichlorodiethylsulphone,  $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{SO}_2$ , leaflets, m. p.  $56^{\circ}$ , b. p.  $183^{\circ}/20$  mm., causes blisters and persistent sores, and also has a lachrymatory, and a slight sternutatory, effect. The physiological activity of these compounds appears to be parallel to the extent to which they suffer hydrolysis (compare Marshall, *J. Amer. Med. Assoc.*, 1919, **73**, 684), for the sulphone reacts partly with boiling aqueous silver nitrate solution. It is obtained from the sulphoxide by oxidation with fuming nitric acid, potassium permanganate, or, most satisfactorily, a solution containing 5—10% of chromic acid and 15—18% of sulphuric acid. The sulphone suffers decomposition at  $230^{\circ}$  when distilled under atmospheric pressure.  $\beta\beta'$ -Dihydroxydiethylsulphone,



is a viscous, somewhat deliquescent syrup, b. p.  $140\text{--}165^{\circ}/15$  mm. Condensation products of the sulphide, sulphoxide, and sulphone with sodium salts of phenols, thiophenols, alcohols, mercaptans, and with aromatic amines have been prepared. Di- $\beta$ -phenylthiol-diethyl sulphide,  $(\text{SPh}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{S}$ , m. p.  $57.5^{\circ}$ . Di- $\beta$ -phenylthiol-diethyl sulphoxide,  $(\text{SPh}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}$ , m. p.  $121.0^{\circ}$ . Di- $\beta$ -

- phenylthioldiethylsulphone,  $(\text{SPh} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{SO}_2$ , m. p.  $104 \cdot 5^\circ$ .  
*Di-β-phenylsulphinyldiethyl sulphoxide*,  $(\text{SOPh} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{SO}$ ,  
 m. p.  $161^\circ$ . *Di-β-phenylsulphinyldiethylsulphone*,  
 $(\text{SOPh} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{SO}_2$ ,  
 m. p.  $164^\circ$ . *Di-β-phenylsulphonyldiethylsulphone*,  
 $(\text{SO}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{SO}_2$ ,  
 m. p.  $235^\circ$ . *Di-β-phenoxydiethyl sulphide*,  $(\text{OPh} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{S}$ ,  
 m. p.  $54 \cdot 2^\circ$ . *Di-β-phenoxydiethylsulphone*,  $(\text{OPh} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{SO}_2$ ,  
 m. p.  $108^\circ$ . *Di-β-p-tolylloxydiethyl sulphide*,  
 $(\text{C}_6\text{H}_4\text{Me} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{S}$ ,  
 m. p.  $78^\circ$ . *Di-β-p-tolylloxydiethylsulphone*,  
 $(\text{C}_6\text{H}_4\text{Me} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{SO}_2$ ,  
 m. p.  $120^\circ$ . *Di-β-o-tolylloxydiethyl sulphide*, m. p.  $46 \cdot 5^\circ$ . *Di-β-α-naphthoxydiethyl sulphide*,  $(\text{C}_{10}\text{H}_7 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{S}$ , m. p.  $94 \cdot 5^\circ$ .  
*Di-β-β-naphthoxydiethyl sulphide*, m. p.  $129^\circ$ . *Di-β-β-naphthoxydiethylsulphone*,  $(\text{C}_{10}\text{H}_7 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{SO}_2$ , m. p.  $151^\circ$ . *Di-β-vanilloxydiethyl sulphide*,  $[\text{OMe} \cdot \text{C}_6\text{H}_3(\text{CHO}) \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2]_2\text{S}$ , m. p.  $131 \cdot 5^\circ$ .  
*Di-β-eugenoxidiethyl sulphide*,  
 $[\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{CH}_2 \cdot \text{CH}_2]_2\text{S}$ ,  
 m. p.  $113 \cdot 5^\circ$ . *Di-β-2:4:6-tribromophenoxydiethyl sulphide*,  
 $(\text{C}_6\text{H}_2\text{Br}_3 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{S}$ ,  
 m. p.  $118 \cdot 5^\circ$ . *Di-β-butylthioldiethyl sulphide*,  
 $(\text{C}_4\text{H}_9 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{S}$ ,  
 m. p.  $17 \cdot 5^\circ$ , b. p.  $222-223^\circ$ . *Di-β-butylthioldiethyl sulphoxide*,  
 $(\text{C}_4\text{H}_9 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{SO}$ , m. p.  $25^\circ$ . *Di-β-butylthioldiethylsulphone*,  
 $(\text{C}_4\text{H}_9 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{SO}_2$ , m. p.  $73 \cdot 7^\circ$ . *Di-β-butylsulphinyldiethyl sulphoxide*,  $(\text{C}_4\text{H}_9 \cdot \text{SO} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{SO}$ , m. p.  $196^\circ$ . *Di-β-butylsulphinyldiethylsulphone*,  $(\text{C}_4\text{H}_9 \cdot \text{SO} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{SO}_2$ , m. p.  $101^\circ$ .  
*Di-β-butylsulphonyldiethylsulphone*,  $(\text{C}_4\text{H}_9 \cdot \text{SO}_2 \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{SO}_2$ ,  
 m. p.  $266 \cdot 5^\circ$ . *Di-β-ethylthioldiethyl sulphide*,  $(\text{SEt} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{S}$ ,  
 m. p.  $17^\circ$ , b. p.  $173-175^\circ$ . *Di-β-ethylthioldiethylsulphone*,  
 $(\text{SEt} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{SO}_2$ , m. p.  $64^\circ$ . *Di-β-ethylsulphonyldiethylsulphone*,  $(\text{SO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{SO}_2$ , m. p.  $223^\circ$ . *Di-β-methylthioldiethylsulphone*,  $(\text{SMe} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{SO}_2$ , m. p.  $77^\circ$ . *Di-β-propylthioldiethyl sulphide*,  $(\text{SPr} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{S}$ , m. p.  $27 \cdot 5^\circ$ , b. p.  $193-195^\circ$ .  
*Di-β-propylthioldiethylsulphone*,  $(\text{SPr} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{SO}_2$ , m. p.  $75 \cdot 5^\circ$ .  
*Di-β-propylsulphonyldiethylsulphone*,  $(\text{SO}_2\text{Pr} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{SO}_2$ ,  
 m. p.  $254^\circ$ . *Di-β-isobutylthioldiethylsulphone*,  
 $(\text{C}_4\text{H}_9 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{SO}_2$ ,  
 m. p.  $94 \cdot 2^\circ$ . *Di-β-sec-butylthioldiethylsulphone*,  
 $(\text{C}_4\text{H}_9 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{SO}_2$ ,  
 m. p.  $15^\circ$ . *Di-β-amylthioldiethyl sulphide*,  $(\text{C}_5\text{H}_{11} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{S}$ ,  
 m. p.  $20^\circ$ . *Di-β-amylthioldiethylsulphone*,  $(\text{C}_5\text{H}_{11} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{SO}_2$ ,  
 m. p.  $91^\circ$ . 4-Phenyl-1:4-thiazan,  $\text{NPh} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{S}$ , m. p.  $108-111^\circ$ . 4-Phenyl-1:4-thiazan 4-oxide,  $\text{NPh} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{SO}$ ,  
 m. p.  $123 \cdot 5^\circ$ . 4-p-Tolyl-1:4-sulphonazan,  
 $\text{C}_6\text{H}_4\text{Me} \cdot \text{N} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{SO}_2$ ,



m. p.  $136.5^{\circ}$ . 4-*o*-Tolyl-1:4-sulphonazan, m. p.  $135^{\circ}$ . Di- $\beta$ -acetoxydiethyl sulphide,  $(\text{OAc}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{S}$ , b. p.  $155\text{--}156^{\circ}/20\text{ mm.}$ ,  $D_{20}^{20} 1.132$ ,  $n_D^{22.5} 1.4720$ . Of the compounds,  $(\text{R}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{S}$ , only those could be obtained in which R=aromatic radicle.

$\beta\beta'$ -Di-iododiethyl sulphide,  $(\text{CH}_2\text{I}\cdot\text{CH}_2)_2\text{S}$ , m. p.  $55\text{--}60^{\circ}$ , the sulphoxide,  $(\text{CH}_2\text{I}\cdot\text{CH}_2)_2\text{SO}$ , m. p.  $104.5^{\circ}$ , and the sulphone,  $(\text{CH}_2\text{I}\cdot\text{CH}_2)_2\text{SO}_2$ , m. p.  $203^{\circ}$ , were obtained from the chloro-derivatives and sodium iodide.

A report on the physiological activity of the above compounds, which is in general slight, is included in the paper. J. K.

**Ethylene Sulphide,  $\text{C}_2\text{H}_4\text{S}$ .** MARCEL DELÉPINE (*Compt. rend.*, 1920, 171, 36—38).—Chloroethyl thiocyanate is decomposed by an aqueous solution of sodium sulphide, giving sodium thiocyanate, sodium chloride, and ethylene sulphide,  $\begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix} > \text{S}$ , a

colourless liquid, b. p.  $55\text{--}56^{\circ}$ ,  $D_4^{20} 1.0368\text{--}1.0342$ ,  $n_D^{18} 1.4914\text{--}1.49001$ . The material slowly polymerises spontaneously, and very rapidly in the presence of some reagents, to give a white solid. With methyl iodide, it gives a crystalline compound having all the characteristics of a sulphinium iodide. This iodide with silver chloride gives a crystalline chloride, yielding a platinumchloride.

W. G.

**Organic Derivatives of Tellurium. II. Constitution of the Dimethyltelluronium Dihaloids.** RICHARD HENRY VERNON (*T.*, 1920, 117, 889—898).

**Production of Acetic Acid from Paracetaldehyde as the Primary Material.** SOCIÉTÉ DES ACIERIES & FORGES DE FIRMINY (*Brit. Pat.* 124195).—Paracetaldehyde is directly converted into acetic acid by electrolytic oxidation, using a porous cathode, for example, gas carbon, and a refractory anode, such as magnetite or platinum. The electrolyte consists of 10% sulphuric acid, in which the paracetaldehyde dissolves to the extent of 10—15%. Any excess is allowed to float on the surface, and dissolves as the oxidation proceeds. Oxidation is facilitated by the addition to the bath of a small quantity of a salt of a metal capable of a plurality of degrees of oxidation, such as manganese, cerium, molybdenum, or vanadium. A high current density is employed, and the acetic acid is allowed to accumulate to a concentration of about 40%, when it is separated from the sulphuric acid by distillation.

G. F. M.

**Manufacture of Ethyl Acetate from Paracetaldehyde as the Primary Material.** SOCIÉTÉ DES ACIERIES & FORGES DE FIRMINY (*Brit. Pat.* 131600).—By adding to the mixture of acetic acid and dilute sulphuric acid produced by the electrolytic oxidation of paracetaldehyde (preceding abstract) a quantity of ethyl alcohol equivalent to the acetic acid which it contains, and distilling the whole on a rectifying apparatus, esterification is effected, and pure ethyl acetate distils. The liquid remaining containing

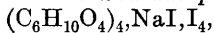
sulphuric acid and a little non-esterified acid and alcohol may be again employed as a basis for a fresh electrolysis. G. F. M.

**Poly-iodide Compounds of Oxalic Esters.** ANTON SKRABAL and ELEONORE FLACH (*Monatsh.*, 1919, **40**, 431—444).—The authors have prepared a number of compounds analogous to the double compound of potassium periodide and ethyl oxalate (compare Skrabal, A., 1917, i, 378) and differing essentially only in degree of stability. These compounds mostly crystallise well and always exhibit a dark colour and metallic lustre, which is frequently combined with pleochroism. They exhibit the characters of the poly-iodides, including the tendency to decompose with liberation of iodine; the pressure at which such decomposition occurs furnishes a measure of the stability.

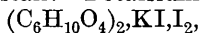
Study of the dissociation equilibria of these compounds shows that the tendency of the iodides of the alkali metals to form compounds with iodine and ethyl oxalate increases in passing from sodium to potassium and then diminishes in passing to rubidium and caesium, ammonium occupying a position near that of potassium; the sodium compound does not correspond in composition with the others. Further, a poly-iodide compound with a bromide as component is of far lower stability than that with the corresponding iodide as component.

The compounds, which have all been prepared either in aqueous solution or in presence of water, apparently belong to the oxonium compounds, but it is undecided whether it is the carbonyl or the ethereal oxygen atom of the oxalic ester which assumes the oxonium valencies. The following compounds are described:

*Compounds of ethyl oxalate: Sodium periodide compound,*

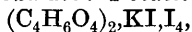


small, reddish-brown crystals. *Potassium periodide,*

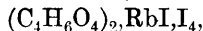


small, brown to violet, highly stable crystals (*loc. cit.*). *Rubidium periodide*,  $(\text{C}_6\text{H}_{10}\text{O}_4)_2, \text{RbI}, \text{I}_2$ , dark brown crystals with metallic lustre. *Ammonium periodide*,  $(\text{C}_6\text{H}_{10}\text{O}_4)_2, \text{NH}_4\text{I}, \text{I}_2$ , bluish-black crystals with metallic lustre, highly stable. *Caesium periodide*,  $(\text{C}_6\text{H}_{10}\text{O}_4)_2, \text{CsI}, \text{I}_2$ , shining, dark brown crystals. *Potassium perbromide*,  $(\text{C}_6\text{H}_{10}\text{O}_4)_2, \text{KBr}, \text{I}_2$ , unstable, shining, golden-brown scales. *Sodium mercuric periodide*,  $(\text{C}_6\text{H}_{10}\text{O}_4)_4, 3\text{NaI}, \text{HgI}_2, \text{I}_4$ , reddish-brown crystals, readily emitting iodine. *Potassium mercuric periodide*,  $(\text{C}_6\text{H}_{10}\text{O}_4)_8, 4\text{KI}, \text{HgI}_2, \text{I}_8$ , reddish-brown crystals. *Potassium cadmium periodide*,  $(\text{C}_6\text{H}_{10}\text{O}_4)_{10}, 6\text{KI}, \text{CdI}_2, \text{I}_{10}$ , shining, brownish-green crystals, readily losing iodine. *Potassium bismuth periodide*,  $(\text{C}_6\text{H}_{10}\text{O}_4)_6, 3\text{KI}, \text{BiI}_3, \text{I}_6$ , reddish-brown powder. In all these compounds, one molecule of ethyl oxalate corresponds with one atom of periodine.

*Compounds of methyl oxalate: Potassium periodide,*

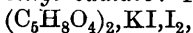


shining, bluish-black crystals. *Rubidium periodide,*



dark crystals. In these compounds, one molecule of the methyl ester corresponds with two atoms of periodine.

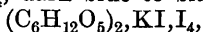
*Compounds of methyl ethyl oxalate: Potassium periodide,*



brown crystals. *Rubidium periodide*,  $(\text{C}_5\text{H}_8\text{O}_4)_2, \text{RbI}, \text{I}_2$ , dark brown crystals. *Ammonium periodide*,  $(\text{C}_5\text{H}_8\text{O}_4)_2, \text{NH}_4\text{I}, \text{I}_2$ , dark blue crystals.

*Compounds of tetraethyl semi-ortho-oxalate: Potassium periodide*,  $(\text{C}_{10}\text{H}_{20}\text{O}_5)_2, \text{KI}, \text{I}_2$ , brownish-violet, stable crystals.

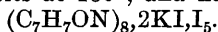
*Compounds of tetramethyl semi-ortho-oxalate: Potassium periodide*,  $(\text{C}_6\text{H}_{12}\text{O}_5)_3, 2\text{KI}, \text{I}_4$ , dark blue to black crystals, and



brownish-black powder, readily emitting iodine.

T. H. P.

**Periodides of Carbonyl Compounds.** A. M. CLOVER (*J. Amer. Chem. Soc.*, 1920, **42**, 1248—1260. Compare A., 1904, i, 322).—Reviewing the isolated instances in the literature of periodides derived from organic compounds free from nitrogen, the author concludes that it is the carbonyl group which is essentially involved in their structure, and suggests the designation “carbonyl periodides,” including among them the periodides of dimethyl- and tetramethyl-pyrones, and of amides, and anilides. Coumarin potassium periodide (Dox and Gaessler, A., 1917, i, 346. Compare Morgan and Micklethwait, T., 1906, **89**, 866) is best purified by the addition of ether to its concentrated solution in alcohol or ethyl acetate, and has the formula  $(\text{C}_9\text{H}_6\text{O}_2)_3, 2\text{KI}, \text{I}_5, \text{H}_2\text{O}$ . *Methyl oxalate potassium periodide*,  $(\text{C}_4\text{H}_6\text{O}_4)_2, \text{KI}, \text{I}_5$ , separates from a mixture of aqueous solutions of its components as fine crystals with a dark bluish-grey lustre, m. p. 55—75°. Benzamide potassium periodide (Moore and Thomas, A., 1914, i, 1130), after crystallisation from ether, melts at 130°, and has the formula



*Succinimide potassium periodide*,  $(\text{C}_4\text{H}_5\text{O}_2\text{N})_4, \text{KI}, \text{I}_2$ , m. p. 141—149°, separates as light brown, lustreless crystals from an alcoholic solution of its components. Succinic anhydride potassium periodide,  $(\text{C}_4\text{H}_4\text{O}_3)_4, \text{KI}, \text{I}_2$ , previously described (*loc. cit.*), separates as crystals with a green lustre from a mixture of ethyl acetate and chloroform. From barbituric acid, two compounds result, according to the proportions of the components mixed in aqueous solution; in one case, yellow crystals,  $(\text{C}_4\text{H}_4\text{O}_3\text{N}_2)_7, 2\text{KI}, \text{I}_5$ , in the other, green crystals,  $(\text{C}_4\text{H}_4\text{O}_3\text{N}_2)_2, 2\text{KI}, \text{I}_5$ , are obtained. *Diethyl-barbituric acid potassium periodide*,  $(\text{C}_8\text{H}_{12}\text{O}_3\text{N}_2)_2, \text{KI}, \text{I}_4$ , from aqueous solutions of its components, forms crystals with a steel-blue lustre, m. p. above 200°. In other cases, there is evidence of formation of compounds, although they cannot be isolated. Thus many organic ketones, anhydrides, esters, etc., dissolve iodine and potassium iodide to a considerable extent, although the solubility of each of these is limited. In this manner, acetone furnishes dark green, needle-shaped crystals of a potassium iodide periodide, and needles with a golden lustre of a sodium iodide periodide. Also, often as a result of fusion or grinding together of the com-

ponents, a strong metallic lustre is developed, and iodine is not so readily lost by volatilisation from the product; in other cases, a lustrous residue is left on evaporation of a solution of the components.

J. K.

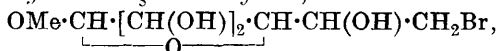
**The Tartaric Acid Compounds of Antimony.** A. BLANCHETIÈRE (*Bull. Soc. chim.*, 1920, [iv], 27, 477—490).—The velocity of solution of freshly-prepared antimony hydroxide in a solution of tartaric acid agrees with Jungfleisch's theory of esterification and not with the formation of a salt. This action, relatively rapid at first, diminishes in velocity very quickly when the ratio of tartaric acid to antimony hydroxide dissolved is about two, but the solution will proceed until this ratio becomes one, after a very long time. Using *d*-tartaric acid, these solutions, when evaporated, give syrupy solutions, which only crystallise with difficulty. If racemic acid is used, the material can be separated, by evaporation, into monoantimonyltartaric acid and ill-defined products. The best method of preparation of this acid is to extract the complexes, richer in tartaric acid, with acetone. Precipitation methods only give a hydrophile gel of the required acid containing a varying excess of tartaric acid.

W. G.

### Compounds and Derivatives of *d*-Glucose-6-bromohydrin.

EMIL FISCHER, BURCKHARDT HELFERICH, and PAAL OSTMANN (*Ber.*, 1920, 53, [B], 873—886).—It is shown that many of the reactions of acetylbromoglucose can be extended to acetyldibromoglucose and that, under suitable conditions, compounds are formed which retain the terminal bromine atom in the place of the hydroxyl group of the sugar molecule. The configuration of all these compounds is the same as that of *d*-glucose.

*β*-Methyl-*d*-glucoside-*ζ*-bromohydrin,

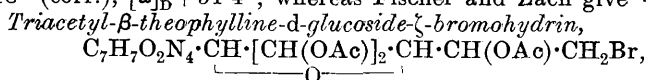


prisms, m. p. about 148° (decomp.),  $[\alpha]_D^{15} - 35 \cdot 12^\circ$  in aqueous solution, is obtained by the action of a methyl-alcoholic solution of ammonia on triacetylmethylglucoside-6-bromohydrin. It is hydrolysed by *N*-hydrochloric acid with the formation of *ζ*-bromoglucose, which, however, could only be obtained as a syrup, but could be identified by conversion into *d*-glucose-ethylmercaptopal-*ζ*-bromohydrin, long, silky needles, m. p. 107° (corr. decomp.),  $[\alpha]_D^{10} + 4 \cdot 92^\circ$  in alcoholic solution.

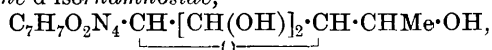
*Tetra-acetyl-d*-glucose-*ζ*-bromohydrin, needles or four-sided prisms, m. p. 127° (corr.) after previous softening, is prepared by treating a hot solution of acetyldibromoglucose in glacial acetic acid with dry silver acetate.

Acetyldibromoglucose is converted, when boiled with water, into a mixture of *ζ*-bromoglucose (identified as the ethylmercaptopal) and anhydroglucose (compare Fischer and Zach, A., 1912, i, 239, 678), which was isolated from the product in the form of its *p*-bromophenylhydrazone, pearly leaflets, m. p. 184° (corr.) after slight previous softening, to a reddish-brown syrup; the substance

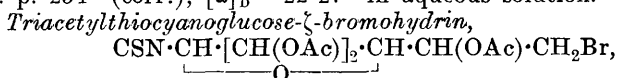
exhibits mutarotation when dissolved in dry pyridine,  $[\alpha]_D^{16}$  having the initial and final values  $-18.89^\circ$  and  $-10.86^\circ$  respectively. It is decomposed by formaldehyde, yielding anhydroglucose, m. p.  $118^\circ$  (corr.),  $[\alpha]_D + 51.4^\circ$ , whereas Fischer and Zach give  $+53.7^\circ$ .



is prepared from acetyldibromoglucose and the silver derivative of theophylline in boiling xylene solution and forms slender needles, m. p.  $193-194^\circ$  (corr.),  $[\alpha]_D^{13} - 9.92^\circ$  in tetrachloroethane solution. It is hydrolysed by methyl-alcoholic ammonia to *β-theophylline-d-glucoside-ζ-bromohydrin*, coarse prisms,  $+2.5H_2O$ ; the anhydrous substance has m. p. about  $217^\circ$  (decomp.) after slight softening,  $[\alpha]_D^{13} - 18.99^\circ$  in aqueous solution,  $[\alpha]_D^{13} - 13.87^\circ$  in *N*-hydrochloric acid solution, mutarotation not being observed in either instance. The triacetyl compound is reduced by zinc dust and acetic acid to *triacetyl-β-theophylline-d-isorhamnoside*, m. p.  $230^\circ$  (corr.), after slight previous softening, which does not exhibit appreciable optical activity when dissolved in tetrachloroethane or glacial acetic acid; it is transformed by a solution of ammonia in methyl alcohol into *β-theophylline-d-isorhamnoside*,



m. p.  $254^\circ$  (corr.),  $[\alpha]_D^{16} - 22.27^\circ$  in aqueous solution.



slender, interwoven needles, m. p.  $164-5^\circ$  (corr.) after previous softening,  $[\alpha]_D^{16} + 16.14^\circ$  in tetrachloroethane solution, is prepared from acetyldibromoglucose and silver thiocyanate, and is converted by boiling alcohol into *triacetyl-d-glucosethiourethane-ζ-bromohydrin*,  $OEt \cdot CS \cdot NH \cdot CH \cdot \underbrace{[CH(OAc)]_2}_O \cdot CH \cdot CH(OAc) \cdot CH_2Br$ , thin,

silky leaflets, m. p.  $128-129^\circ$  (corr.),  $[\alpha]_D^{15} + 10.27^\circ$  in tetrachloroethane solution. H. W.

### Biochemical Preparation of Sucrose from Gentianose.

EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1920, **171**, 11-15).—By the action of emulsin, freed as completely as possible from invertase, on a solution of gentianose, a mixture of dextrose and sucrose was obtained. The dextrose was converted into *β*-methyl glucoside and the sucrose isolated in a pure crystalline state.

W. G.

### The Action of Radium Radiation on Sucrose and Agar.

A. FERNAU (*Biochem. Zeitsch.*, 1920, **102**, 246-251).—Sucrose is inverted by the action of radium radiation. Agar submitted to the same influence liquefies with the production of sugars (most probably galactose and arabinose) which reduce strongly Fehling's solution. The chemical change in both cases is due to the primary action of the radium. S. S. Z.

**Alteration of Volume in the Inversion of Sucrose.** N. SCHOORL (*Zeitsch. Nahr. Genussm.*, 1920, **39**, 113—121).—A discussion on the contraction in volume occurring when sucrose is hydrolysed by acid. The contraction for one gram-molecule of sucrose and one gram-molecule of water is 6.9 c.c., which corresponds approximately with 0.5 c.c. for 26 grams of sucrose per 100 c.c. of water.

W. P. S.

**The Hydrolysis of the Polysaccharides.** E. HILDT (*Compt. rend.*, 1920, **170**, 1505—1507. Compare A., 1919, ii, 84).—A further examination of the use of the mixture of sulphuric acid and sodium benzenesulphonate in the molecular proportions of 1:2 for the hydrolysis of disaccharides. It is shown that both dextrose and galactose are unaltered by this reagent, retaining their rotatory and reducing powers. Non-lævulosic sugars, such as lactose, maltose, or glycogen, are not hydrolysed at the ordinary temperature by this catalyst, but in the case of sugars, such as sucrose, raffinose, or inulin, the lævulose is completely split off after the lapse of a considerable time at the ordinary temperature, or in less than one hour at 95—98° in the case of sucrose and raffinose.

W. G.

**Iron Salt of Carbohydrate-Phosphoric Acid.** KARL SCHWEIZER (*Mitt. Lebensmit. Hyg.*, **11**, 16—23; from *Chem. Zentr.*, 1920, i, 881).—Iron zymophosphate,  $C_6H_{10}O_4(PO_4Fe)_2$ , is a greyish-green, tasteless, and odourless powder, which decomposes without melting at 200°. For its preparation, a solution of sucrose (100 grams) in distilled water (250 c.c.) is treated with commercial expressed yeast (150 grams) and toluene (1 c.c.); after ten minutes, a solution of disodium phosphate (80 grams) in water (300 c.c.) is added, and, after four hours, the yeast is removed, preferably by centrifuging. The liquid is heated to 60°, and, after removal of precipitated albumin, is treated with a saturated solution of ferrous chloride (14 grams). The separation of the precipitate is facilitated by the addition of an equal volume of alcohol (90%) to the solution; it is purified by repeated grinding with water. The salt is decomposed by hydrochloric, nitric, sulphuric, and acetic acids, the iron passing thereby into the ionised state; with sodium hydroxide, a precipitate of iron hydroxide is formed. The salt is decomposed in the stomach, both iron and phosphoric acid being converted into forms which are readily absorbed.

H. W.

**Hydrogen Peroxide as Solvent.** MAX BAMBERGER and JOSEF NUSSBAUM (*Monatsh.*, 1919, **40**, 411—416).—Concentrated aqueous hydrogen peroxide solutions, and in higher degree the almost anhydrous peroxide obtained from these by freezing, serve as excellent solvents for many organic compounds. Among the latter are compounds rich in hydroxyl groups, and the higher the molecular weight of these compounds, the more concentrated must be the peroxide solution necessary to effect solution.

For instance, 60% aqueous hydrogen peroxide solution dissolves

starch, giving solutions which are viscous or dough-like, according to the concentration. Cellulose and its decomposition products are also soluble, and the less the extent to which the cellulose has been altered, the greater the concentration of the peroxide required for solution. From these solutions, precipitants, such as water, throw out the cellulose in chemically modified form, and the solutions themselves undergo gradually increasing change in properties. Cellulose wool, as used for preparing cellulose nitrate, dissolves to the extent of 25%, the tenacious dough thus formed becoming more and more mobile when kept out of contact with atmospheric moisture. The products precipitated from these solutions differ from those obtained by the action of sulphuric acid on cellulose, no substance coloured blue by iodine being formed.

With peroxide solution weaker than that necessary for solution, cellulose swells, and cotton wool thus treated shows under the microscope swollen fibres with a greatly diminished lumen; flattened or damaged portions of the fibres dissolve the more readily, the double refraction and the visibility of the fibres disappearing as dissolution proceeds.

In spite of its negative heat of formation, anhydrous hydrogen peroxide is not explosive, and a large quantity of it cannot be exploded by means of a 2-gram mercury fulminate cap. In conjunction with certain organic compounds, however, the peroxide yields powerful explosives capable of technical application.

Sugars and proteins also dissolve in concentrated hydrogen peroxide solutions. The latter produce no apparent change in pure, white wool, but when this is withdrawn and well washed with water, the fibres exhibit considerable strength, and are almost as elastic as rubber; after being dried, these fibres completely lose their elasticity.

The action of the peroxide on substances dissolved in it seems to be of the nature of a decomposition or depolymerisation. Thus paraformaldehyde yields formaldehyde, or, under some conditions, formaldehyde peroxide (compare Legler, A., 1883, 860; 1886, 327; Nef, A., 1898, i, 111).

In working with concentrated hydrogen peroxide solutions, great cleanliness is necessary, since contamination with catalysts, for instance, iron, manganese, or lead, causes very vigorous decompositions, which are accompanied by generation of heat, and may produce ignition. Such mixtures burn in the air with hissing, like smokeless powder. Ignition may be produced by sprinkling powdered lead peroxide or iron pyrites on the peroxide solution.

T. H. P.

### **Constitution of Cellulose. I. Acetolysis of Ethyl Cellulose.**

KURT HESS and WALTER WITTELSBACH (*Zeitsch. Elektrochem.*, 1920, **26**, 232—251).—The various formulæ proposed for cellulose are discussed. The formation of  $\omega$ -bromo-5-methylfurfuraldehyde from cellulose and from dextrose (Fenton and Gostling, T., 1901, **79**, 361, 807) suggests that, contrary to the formulæ of Green (T., 1906, **89**, 811), cellulose contains dextrose residues in the same

form as dextrose itself. The production of lævoglucozan from starch as readily as from cellulose, to which it bears no resemblance (Pictet and Sarasin, A., 1918, i, 58), discounts the idea of any constitutional similarity between lævoglucozan and cellulose, but suggests that it owes its origin to dextrose residues present in each. In confirmation of the view that the hydrofuran ring of lævoglucozan is not present in cellulose, it is shown that ethyl cellulose, on distillation under reduced pressure, gives no ethyl lævoglucozan, but only a small proportion of an oily product. As a basis for a new formula for cellulose, it is pointed out that all five hydroxyl groups of dextrose are etherifiable, as evidenced by the tannins (E. Fischer, A., 1913, i, 1352; 1919, i, 278) and certain bisaccharides (Haworth and Leitch, T., 1918, **113**, 188; 1919, **115**, 809; Irvine and Dick, T., 1919, **115**, 593). Formulæ, too complicated to be reproduced, are therefore discussed in which the hydroxyl groups of a dextrose or cellobiose molecule are etherified by molecules of dextrose or cellobiose. In order to reach some decision between the numerous possibilities of such an arrangement, the work of Ost (A., 1906, i, 560) and of Madsen (*Diss.*, Hanover, 1917) on the production of cellobiose acetate and dextrose penta-acetate is reviewed, in conjunction with a repetition of their experiments. The conclusion is that the probable maximum yield of each from ten parts of air-dry cellulose is 6.2 grams of cellobiose acetate and 12 grams of dextrose penta-acetate. It has not been possible to attain the higher yields recorded by Ost in certain experiments. The dextrins, which occur in the form of acetates when the maximum proportion of cellobiose acetate is not reached, are looked on as mixed partial degradation products of the cellulose molecule, resulting from the removal by hydrolysis in a variety of ways of one or more dextrose or cellobiose residues. The formula  $\text{OX} \cdot \text{CH} \cdot [\text{CH}(\text{OX})]_2 \cdot \text{CH} \cdot \text{CH}(\text{OX}) \cdot \text{CH}_2 \cdot \text{OX}$ , in which X represents

the residue,  $\text{CH} \cdot [\text{CH}(\text{OH})]_2 \cdot \text{CH} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$ , requires that

9.38 grams of cellulose should give 6.42 grams of cellobiose acetate and 12.51 grams of dextrose penta-acetate, whilst the other alternatives require widely different quantities. Although the arbitrary nature of this formula, in view of the evidence available, is recognised, it is adopted as a working basis. In accordance with it, Denham and Woodhouse (T., 1913, **103**, 1735; 1914, **105**, 2357) considered dextrose to be among the products of hydrolysis of methyl cellulose. Evidence of a similar nature is presented from the results of hydrolysis of an ethyl cellulose, containing 2.5 ethyl groups per dextrose residue (or 3 per residue with free hydroxyl groups in the formula), under conditions of acetolysis much milder than those usual in the case of cellulose, and such that hydrolysis of ethoxy-groups, as might occur with hydrochloric acid, did not occur. It follows from the formula that the ethoxy-numbers of the ethyl dextrins produced in the form of acetates as intermediate products of acetolysis will always be less than that of the original ethyl cellulose, and, a point not explained by previous



formulae, when degradation has proceeded sufficiently far, less than that of the ethyl glucoses, which, in the form of acetates, will also have a lower ethoxy-number than ethyl cellulose. Repeated experiments uniformly confirmed this, and the ethoxy-number of the sugar portion at the outset (36.5) was much higher than that for diethyl triacetylglucose (21.6%), the formation of which the older formulae would suggest. The marked difference between cellulose and its derivatives, for example, nitrate, acetate, and the products obtained by the action of acids, alkalis, or zinc or copper ammonium compounds, is accounted for by considering such derivatives to be derived from the above simple formula, which is taken as representing hydrocellulose (for which the name cellulose is now proposed), whilst cellulose is a condensation product of a number of such molecules. The results of Stern (T., 1904, **85**, 336), Stein (*Diss.*, Dresden, 1911), and Ost (A., 1913, i, 833) show that little, if any, elimination of water can be assumed in this condensation, and it is suggested that the separate molecules are united through residual affinities of hydroxyl groups. The ability of alcohols of all kinds (Grün and others, A., 1908, i, 934; 1910, i, 352; Vanino and Hartl, A., 1906, i, 785), of dextrose (Lippmann, *Chemie der Zuckerarten*, I, 549), and of its esters and glucosides (Fischer and Hess, A., 1912, i, 415) to form double compounds with metallic salts is in accord with this idea, which leads to a simple explanation of the disintegrating effect of zinc chloride, ammonia, and similar reagents on cellulose as due to their competition for the residual valencies responsible for the complexity of the cellulose molecule. Ethyl cellulose is a derivative of cellulose, since its acetolysis takes place under much less stringent conditions than that of cellulose, and the heat of reaction is slight; the contrast in this respect with cellulose is only partly accounted for by the greater number of hydroxyl groups in cellulose, and is chiefly due to the difference in distribution of valency in the two cases. It is also suggested that the physical characteristic of cellulose as a hollow thread is reproduced in the arrangement of the cellulose molecules in the cellulose complex, and that this complex may be partly broken down by mechanical means, for example, in the case of "totgemahlener" cellulose, which represents a stage of disintegration approaching the less profound of those produced chemically. Similar considerations may apply to the molecules of hemicelluloses, protein, and caoutchouc, but the case of starch is left open. J. K.

**Cellulose and its Esters. I. Fractional Precipitation of Cellulose Nitrates.** J. DUCLAUX and (MME) E. WOLLMAN (*Bull. Soc. chim.*, 1920, [iv], **27**, 414—420).—By fractional precipitation of cellulose nitrate from its solution in acetone by aqueous acetone or water, it is possible to divide it into a number of fractions which have widely different viscosities in 2% acetone solution. By repeating this process with the extreme fractions, fractions were ultimately obtained the viscosities of which in acetone solution were as 46:1, and at one end a cellulose nitrate was obtained which in

1% acetone solution was as viscous as glycerol. These various fractions have not undergone any change in the fractionation, since they obey the law of mixtures in so far as their viscosities are concerned. Further, the nitrogen content of the different fractions of one and the same operation is sensibly the same. A better method of separation of the fractions rather than by fractional precipitation is probably by the use of a series of ultra-filters. The different cellulose nitrates can best be characterised and differentiated by osmotic pressure measurements. W. G.

**The Viscosity of Solutions of Nitrocellulose in Mixtures of Acetone and Water.** IRVINE MASSON and ROBERT MCCALL (*T.*, 1920, **117**, 819—823).

**The Viscosity of Solutions of Cellulose Nitrate in Ether-Alcohol.** WILLIAM HOWIESON GIBSON and ROBERT MCCALL (*J. Soc. Chem. Ind.*, 1920, **39**, 172—176T).—With a given cellulose nitrate, the viscosity of its solution in an ether-alcohol mixture is dependent on the ratio of ether to alcohol, and reaches a minimum value at a definite ratio. This optimum ratio is independent of the concentration of the cellulose nitrate, but is affected by the nitrogen content.

The optimum composition of an ether-alcohol solvent for a cellulose nitrate is not affected by the addition of glyceryl nitrate. Glyceryl nitrate, when added to solutions of cellulose nitrate in ether-alcohol, tends to increase the viscosity of the solution. W. G.

**Measurement of the Viscosity of Pyroxylin Solutions.** E. F. HIGGINS and E. C. PITMAN (*J. Ind. Eng. Chem.*, 1920, **12**, 587—591).—Efflux viscosimeters are only suitable for pyroxylin solutions of low viscosity, and the steel ball viscosimeter (*T.*, 1920, **117**, 473) for those of very high viscosity. The most generally applicable instrument is Stormer's viscosimeter, in which the viscosity is calculated from the speed of rotation of a cylinder in the liquid. When absolute viscosities are plotted as ordinates against the times of 100 revolutions as abscissæ, the points will be found to lie along a straight line. The equation is therefore of the type  $V = At + B$ , where  $B$  is the value of  $V$  when  $t = 0$ . In the case of the particular instrument used, when  $t = 0$ ,  $V = -25 = B$ . By substituting this value for  $B$  at any point of the curve, the value for  $A = 4.6$ . The equation for calculating absolute viscosity from the observed readings when a 150-gram counterweight was used was therefore  $V = 4.6t - 25$ . The speed of revolution varies directly with the magnitude of the counterweight. The correction for the friction factor is practically a constant over a viscosity range of 20 to 500 centipoises. C. A. M.

**The Neutral Hydrolysis of Guncotton. The Alkaline Hydrolysis of Guncotton.** E. KNECHT and B. R. BOSTOCK (*J. Soc. Chem. Ind.*, 1920, **39**, 163—165T).—When guncotton is heated with water in a sealed tube at 190°, it undergoes hydrolysis, the

guncotton disappearing and a pale straw-coloured liquid being left. The rate of hydrolysis depends on the relative proportions of guncotton and water used. If the temperature is lowered by more than about  $2^{\circ}$ , the hydrolysis is extremely slow, and if it is raised  $10-15^{\circ}$ , a considerable amount of charring takes place. The amount of gas given off by heating 0.5 gram of guncotton with 25 c.c. of water for half-an-hour at  $190^{\circ}$  is 99 c.c. The gas consists of carbon monoxide and dioxide and nitrous oxide and nitrogen. Some hydrocyanic acid and ammonia are found in the solution. Of the 13.05% of nitrogen originally present in the guncotton, 10.24% is found as nitrous oxide and nitrogen, 0.43% as hydrogen cyanide, 1.20% as ammonia, 0.12% as nitrate, and 0.27% undetermined.

When guncotton is dissolved in aqueous sodium hydroxide on a water-bath, it is found that 65% of the total nitrate nitrogen is reduced to nitrite in order to provide the oxygen for the organic oxidation products which result from the hydrolysis. The extent of this reduction is nothing like so great in the alkaline hydrolysis as in the neutral aqueous hydrolysis.

W. G.

**Non-existence of Valence and Electronic Isomerism in Hydroxylammonium Derivatives.** ARTHUR MICHAEL (*J. Amer. Chem. Soc.*, 1920, **42**, 1232—1245).—A theoretical paper in which the alkyl hydroxylammonium salts are discussed with regard to their formation and constitution. The author comes to the conclusion that since isomeric trialkyl-hydroxylammonium salts and trialkyl-dialkyloxyammonium derivatives are unknown, there is no experimental evidence in this field to support Werner's ammonium or co-ordination hypotheses, or any modification of them. Neither are any facts known which substantiate electronic conceptions, or the existence of "electromers" in this group of compounds.

J. F. S.

**Salts of *N*-Methylhexamethylenetetramine.** R. TSCHUNKE (U.S. Pat. 1336709).—Salts of *N*-methylhexamethylenetetramine are produced by treating a mixture of formaldehyde and ammonia with methylating agents (such as methyl sulphate, methyl thiocyanate, methyl nitrate, methylamine thiocyanate, or chlorobromomethane) in the presence of acid anions, heating for some time, and allowing the product to crystallise. The thiocyanate, metaborate, dichromate, ferrocyanide, picrate, perchlorate, chlorate, nitrate, sulphate, acetate, and salicylate are mentioned, and details of the methods of making them are given.

CHEMICAL ABSTRACTS.

**The Metallic Dithiocarbamates, especially those of Cobalt and Nickel.** LOUIS COMPIN (*Bull. Soc. chim.*, 1920, [iv], **27**, 464—469. Compare Delépine, *ibid.*, 1908, [iv], **3**, 643).—The author has prepared certain dithiocarbamates of cobalt, nickel, and copper by double decomposition of salts of these metals with the sodium dithiocarbamates. The cobaltic salt obtained is always accompanied by a certain amount of cobaltous salt, and in one or two cases it was possible to isolate the latter salts. The following

salts were prepared: *Sodium, cobaltic, and nickel methyldithiocarbamates; sodium and cobaltic ethyldithiocarbamates; sodium, cobaltic, and nickel propyldithiocarbamates.* These sodium and nickel salts were all crystalline, but the cobaltic salts were only obtained with difficulty. *Copper dimethyldithiocarbamate; cobaltic, nickel, and copper diethyldithiocarbamates; potassium cobaltic, nickel, and copper dipropyldithiocarbamates; cobaltic diallyldithiocarbamate; cobaltic di-isobutyldithiocarbamate; cobaltic, cobaltous, nickel, and copper di-isoamyldithiocarbamates; potassium, cobaltic, and cobaltous dibenzylthiocarbamates; sodium and cobaltic methylphenyldithiocarbamates; sodium and cobaltic piperidyldithiocarbamates; and cobaltic tetrahydroisoquinolyldithiocarbamate.* W. G.

### Is the Direct Synthesis of Carbamide by Urease Possible ?

TH. J. F. MATTAAR (*Rec. trav. chim.*, 1920, **39**, 495—498).—The author has repeated Barendrecht's work (this vol., i, 195) on the action of the urease in soja flour on ammonium carbonate, and has also used a sample of urease prepared by the method of van Slyke and Cullen (A., 1914, ii, 822), and finds no evidence that the synthesis of carbamide takes place; but, on the contrary, finds that any carbamide introduced into such a solution of ammonium carbonate containing the urease is destroyed. W. G.

**Arsine Thiocyanates and certain other Organic Derivatives of Arsenic.** WILHELM STEINKOFF and WALTER MIEG (*Ber.*, 1920, **53**, [B], 1013—1017).—Attempts have been made to prepare arsine thiocyanates of the general form,  $RA_s(SCN)_2$  and  $R_2As \cdot SCN$ , by the action of solutions of sodium thiocyanate in acetone on the corresponding chlorides. Under these conditions, methylarsine dichloride gave only products which were extremely readily decomposed by moisture with the production of amorphous, yellow substances, and which could not be distilled even under diminished pressure, whilst arylarsine dichlorides could not be caused to react in the desired sense. On the other hand, products of the type  $R_2As \cdot SCN$ , in which R is an alkyl or aryl radicle, could be obtained in several cases as fairly stable substances. Improved methods of preparing some arsine chlorides are given and certain new members of this series are described.

Ethyldichloroarsine, b. p. 145—150°, is conveniently prepared from arsenic trichloride and mercury diethyl, and is converted by potassium hydroxide in the presence of benzene and a little water into ethylarsine oxide,  $AsEt_2O$ , colourless oil, b. p. 158°/10 mm., which readily becomes oxidised on exposure to air. *isoAmyldichloroarsine*, from *isoamylarsinic acid* and phosphorus trichloride in chloroform solution, is a colourless liquid, b. p. 88·5—91·5°/15 mm., which is decomposed by water.  *$\alpha$ -Naphthyldichloroarsine* has m. p. 68°. Cacodyl chloride is obtained by the action of sodium hypophosphite on cacodylic acid in the presence of concentrated hydrochloric acid, and has b. p. 106·5—107°; it does not fume on

exposure to the atmosphere, and is rapidly converted by dry air into a crystalline oxidation product. *Cacodyl thiocyanate*,  $\text{AsMe}_2\cdot\text{SCN}$ , b. p.  $92^\circ/17$  mm., is a colourless oil which gradually becomes yellow when preserved. *Phenyldimethylarsine dichloride*,  $\text{AsMe}_2\text{PhCl}_2$ , m. p.  $134^\circ$  (decomp.), is prepared by the addition of chlorine to phenyldimethylarsine and is decomposed at  $180^\circ$ , yielding *phenylmethylchloroarsine*, b. p.  $229\text{--}232^\circ$ . *Diphenylarsine thiocyanate* has b. p.  $230\text{--}233^\circ/22\text{--}23$  mm.; it is decomposed by water with the elimination of the thiocyno-group.

H. W.

**Chemical Actions of Penetrating Radium Radiation. XI. Influence of Penetrating Rays and of Ultra-violet Light on Toluene alone and in Presence of Water.** ANTON KAILAN

(*Monatsh.*, 1919, **40**, 445—466. Compare A., 1918, i, 209).—Exposure of toluene in the dark for about two years to the action of the radiation from a preparation containing 0.080 gram of radium in a glass envelope 1 mm. in thickness, results in attack of less than 0.25% of the toluene, the products formed including benzaldehyde, benzoic acid, and apparently formic acid. The increase in the density of the toluene and the weight of the residue left on evaporation indicate that the principal product of the reaction consists, not of benzoic acid, but of a yellow, viscous mass composed presumably of hydrocarbons and of condensation products of benzaldehyde (compare Ciamician and Silber, A., 1912, i, 174). Changes of similar nature and order of magnitude are produced in toluene, exposed for twenty-two hours to the radiation from a quartz mercury lamp at a distance of 8—9 cm.

The action of radium radiation on toluene in presence of water yields three times as much acid as in absence of water, benzoic and formic acids being produced, together with a non-acid residue. As regards the action on toluene of the radiation from a quartz mercury lamp, this is not increased by the presence of water to the same extent as the action of radium radiation, but oxalic acid is then produced, as well as benzoic and formic acids. T. H. P.

**The Catalysing Action of Aluminium in the Preparation of Chlorobenzenes.** JEAN MEUNIER (*Compt. rend.*, 1920, **170**, 1451—1452).—In the preparation of chlorobenzene, one part of aluminium to one thousand of benzene acts as a very satisfactory catalyst, the absorption of chlorine proceeding smoothly. The action should be stopped when the density of the liquid reaches 1.008.

W. G.

**The Replacement of Substituents in the Benzene Nucleus.** A. F. HOLLEMAN and A. J. DEN HOLLANDER (*Rec. trav. chim.*, 1920, **39**, 435—480. Compare A., 1916, i, 22; 1918, i, 216).—The eleven dichlorodinitrobenzenes have been prepared and their behaviour in the presence of sodium methoxide studied. Three of these compounds are new.

By hydrolysis of 3:6-dichloro-2-nitroacetanilide, and subsequent

replacement of the amino-group by a nitro-group by the method of Körner and Contardi (compare A., 1914, i, 263), 1:4-dichloro-2:3-dinitrobenzene, m. p.  $103^{\circ}$ , is obtained, which is identical with Jungfleisch's  $\beta$ -dichlorodinitrobenzene obtained in the preparation of 1:4-dichloro-2:6-dinitrobenzene (compare *Ann. Chim. Phys.*, 1868, [iv], 15, 259).

1:4-Dichloro-2:5-dinitrobenzene, m. p.  $119^{\circ}$ , is prepared by the hydrolysis of 3:6-dichloro-4-nitroacetanilide, and replacement of the amino-group by a nitro-group. Alternatively, this compound may be prepared by nitrating 4-chloro-3-nitroacetanilide, hydrolysing the product, diazotising the amine, and introducing a chlorine atom by the Gattermann reaction. The authors consider that the compounds described under the name 1:4-dichloro-2:5-dinitrobenzene by Morgan and Norman (T., 1902, 81, 1378, 1382), Hartley and Cohen (T., 1904, 85, 868), and Nason (A., 1919, i, 10) are either impure or different isomerides.

By the chlorination of 2:5-dinitroaniline by hydrochloric acid and potassium chlorate, a mixture of two compounds, which were not isolated, was obtained. This mixture was diazotised, and the resulting diazonium salts submitted to the Gattermann reaction. By this means, 1:4-dichloro-2:5-dinitrobenzene mixed with a small amount of 1:2-dichloro-3:6-dinitrobenzene, m. p.  $60^{\circ}$ , was obtained. Several attempts to prepare the last-named compound by other methods were unsuccessful.

From a qualitative and quantitative study of the action of sodium methoxide on the chloronitrobenzenes, it is shown that the activity of a replaceable chlorine atom is increased considerably by the introduction of a nitro-group into the para- or ortho-positions, and that the activity of a nitro-group becomes greater on the introduction of a chlorine atom, more particularly in the meta-position. The introduction of a second nitro-group into the chloronitro- and dichloronitro-benzenes renders the chlorine atoms in the meta-position to the nitro-group already present inactive. On the other hand, when the two nitro-groups are in a meta-position to one another, it is always a chlorine atom which is attacked.

W. G.

**Nitration of *m*-Nitrotoluene.** M. D. MARQUEYROL, M. G. A. KOEHLER, and JOVINET (*Bull. Soc. chim.*, 1920, [iv], 27, 420—424). —By the nitration of *m*-nitrotoluene with a mixture of 16 parts of sulphuric acid (96%) and 2.25 parts of nitric acid (88%) for eight hours at  $100^{\circ}$ , a mixture of three trinitrotoluenes, namely, 2:3:4-, 3:4:6-, and 2:3:6- or 2:3:5-trinitrotoluenes, is obtained.

W. G.

**Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. II. The Dinitrotoluenes.** JAMES KENNER and MICHAEL PARKIN (T., 1920, 117, 852—859).

**2:3:6-Trinitrotoluene: a New Synthesis.** OSCAR LISLE BRADY and ARTHUR TAYLOR (T., 1920, 117, 876—880).

**Trinitration of *o*-Xylene.** M. D. MARQUEYROL and P. LORLETTE (*Bull. Soc. chim.*, 1920, [iv], 27, 424—426).—By passage through its mono- and dinitro-derivatives without purification of these, but using fresh nitration mixtures at each stage, the two trinitro-*o*-xylenes, previously described by Crossley and Renouf (compare T., 1909, 95, 202), were obtained from *o*-xylene. W. G.

**Preparation of Condensation Products from *N*-Arylsulpho-derivatives of Aromatic Aminosulphonic Acids.** SOCIETY OF CHEMICAL INDUSTRY IN BASEL (D.R.-P. 319713; from *Chem. Zentr.*, 1920, ii, 777).—Formaldehyde is caused to react with *N*-arylsulphonyl derivatives of aminosulphonic acids of the benzene or naphthalene series. Examples are given of the condensation of *p*-toluenesulphonylsulphanilic acid in sodium carbonate solution, of *p*-toluenesulphonyl-1-aminonaphthalene-6-sulphonic acid in dilute sodium carbonate solution, and of amino-*p*-toluenesulphonyl-1-aminonaphthalene-6-sulphonic acid in acetic acid solution with formaldehyde. The products are soluble in water, precipitate albumin, and tan hide. H. W.

**The Constitution of Anthracene.** K. VON AUWERS (*Ber.*, 1920, 53, [B], 941—944).—During recent years, a variety of chemical evidence in favour of the orthoquinonoid structure of anthracene has been adduced, and this is now supplemented by physical evidence. If this mode of formulation be correct, the system would contain a continuous chain of four conjugated double bonds which could not neutralise one another, and although this system is twice broken, and by reason of its position in the rings would probably not exhibit its full activity, it should, nevertheless, show strong exaltation of the refractive and the dispersive power. On the other hand, a compound with a para-linking in the central ring should show, at most, little exaltation, since the benzene nuclei are so disposed that active conjugations are not existent, and the para-bond is known in analogous cases to have little, if any, effect. Anthracene itself is unsuitable for investigation on account of its high melting point, but 9-isoamylanthracene has been investigated and found to exhibit very marked optical exaltation, which is very much less in evidence in the case of its dihydro-derivative, which behaves precisely as if it contained two benzene nuclei.

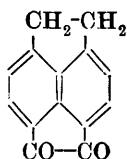
The following constants are recorded: 9-isoamylanthracene, m. p. 58°, (i)  $D_4^{75.5}$  0.9982,  $n_D^{75.5}$  1.62353,  $n_D^{71.5}$  1.63475,  $n_D^{75.5}$  1.67008, (ii)  $D_4^{44}$  0.9987,  $n_D^{71.1}$  1.62491,  $n_D^{71.1}$  1.63636,  $n_D^{71.1}$  1.67152. Dihydro-9-isoamylanthracene, (i) b. p. 202°/23 mm.,  $D_4^{45.1}$  1.0022,  $D_4^{20}$  1.025,  $n_D^{45.1}$  1.56091,  $n_D^{45.1}$  1.56584,  $n_D^{45.1}$  1.58047,  $n_D^{20}$  1.5771, (ii) b. p. 201—205°/17 mm.,  $D_4^{44}$  0.9940,  $D_4^{20}$  1.016,  $n_D^{44.4}$  1.55791,  $n_D^{44.4}$  1.56261,  $n_D^{44.4}$  1.57651,  $n_D^{20}$  1.5736. H. W.

**Derivatives of Acenaphthene.** KARL FLEISCHER and PAUL WOLFF (*Ber.*, 1920, 53, [B], 925—931).—The recent publication of Mayer and Kaufmann (this vol., i, 301) on a similar topic has

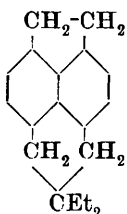
caused the authors to communicate the results obtained by themselves in this field.

A *diacetylacenaphthene*, colourless needles, m. p.  $146^{\circ}$ , has been isolated from the less volatile products obtained in the preparation of 5-acetylacenaphthene. The latter readily condenses with benzaldehydes to yield well-crystallised benzylidene derivatives, of which the *o*-chlorobenzylidene compound forms yellow prisms, m. p.  $113^{\circ}$ . 5-Acetylacenaphthene is reduced to 5-ethylacenaphthene, colourless, mobile oil, b. p.  $158^{\circ}/13$  mm., m. p.  $42.5-43^{\circ}$ , D  $1.0407$ ,  $n$   $1.6117$ , by amalgamated zinc and hydrochloric acid (compare Mayer and Kaufmann, *loc. cit.*). The latter condenses with acetyl chloride in the presence of aluminium chloride to yield 6(?)*-acetyl-5-ethylacenaphthene*, m. p.  $110.5^{\circ}$ , which gives nicely crystalline benzylidene derivatives with aromatic aldehydes, and is reduced by Clemmensen's method to 5:6(?)*-diethylacenaphthene*, pale yellow oil, b. p.  $182^{\circ}/14$  mm., m. p.  $10-11^{\circ}$ .

The author's attempts to introduce a second ethylene bridge in the *peri*-position in the acenaphthene molecule date back to 1911; for this purpose, oxalyl chloride does not appear to be a suitable reagent, but better results can be obtained with oxalyl bromide, which yields the substance (annexed formula), yellow crystals, m. p.  $226^{\circ}$  after slight previous softening and darkening. (The authors propose to call the substance *pyracenechemiquinone* and the parent hydrocarbon *pyracene*.)



Bromoacetyl bromide condenses with acenaphthene in the presence of aluminium chloride to yield 5-bromoacetylacenaphthene, pale grey, crystalline powder, m. p.  $180^{\circ}$ , and a substance, small, yellow needles, m. p.  $94-96^{\circ}$ , which could not be definitely identified.



A hydrocarbon closely allied to the hypothetical pyracene has been isolated by the reduction, by phosphorus and hydriodic acid, of 2:2-diethylperi-acenaphthindan-1:3-dione (Freund and Fleischer, A., 1910, i, 490; 1913, i, 1073), which yields 2:2-diethylperiacenaphthindane (annexed formula), centimetre-long crystals, m. p.  $93-95^{\circ}$ . H. W.

**New Synthesis of Perylene.** FRITZ HANS GIG and ALOIS ZINKE (*Monatsh.*, 1919, **40**, 403-404).—Perylene may be obtained in good yield by heating 2:2'-dihydroxy-1:1'-dinaphthyl to a high temperature ( $400-500^{\circ}$ ) with a halogen compound of phosphorus ( $\text{PCl}_5$ ,  $\text{PCl}_3$ ,  $\text{POCl}_3$ ,  $\text{PBr}_5$ ), addition of phosphorous acid being of advantage. Hydrogen phosphide and small proportions of free phosphorus are formed during the reaction. T. H. P.

**New Derivatives of Perylene.** ALOIS ZINKE and ERNA UNTERKREUTER (*Monatsh.*, 1919, **40**, 405-410).—*Perylene hexa-*



*hydride*,  $C_{20}H_{18}$ , prepared by heating perylene with hydriodic acid and red phosphorus at  $200-210^{\circ}$ , forms almost colourless, rhombohedral plates, m. p.  $183-184^{\circ}$  (uncorr.), which gradually turn yellow, especially in the light. It appears to sublime unchanged when very cautiously heated, but yields perylene when distilled over heated asbestos. It dissolves in warm concentrated sulphuric acid, giving a red solution.

*Trinitroperylene*,  $C_{20}H_9(NO_2)_3$ , prepared by the action of nitric acid (D 1.10) at  $100^{\circ}$ , crystallises in needles, decomposes at about  $365^{\circ}$ , and yields a violet-red solution in warm, concentrated sulphuric acid.

*Tetranitroperylene*,  $C_{20}H_8(NO_2)_4$ , prepared by boiling perylene with concentrated nitric acid (D 1.4), forms deep brick-red leaflets and darkens at above  $300^{\circ}$ . With warm sulphuric acid, it gives a red solution.

The oxidation of perylene to perylenequinone is effected readily by boiling the hydrocarbon with aqueous chromic acid solution.

*Perylenequinol dibenzoate*,  $C_{20}H_{10}O_2Bz_2$ , prepared from perylenequinone by Scholl and Mansfeld's method (A., 1910, i, 494), forms bundles of yellow needles, m. p.  $295-296^{\circ}$  (uncorr.), and yields a reddish-yellow solution with concentrated sulphuric acid.

*Dibromoperylenequinone*,  $C_{20}H_8O_2Br_2$ , crystallises in needles or leaflets, decomposes at about  $412^{\circ}$ , and dissolves in concentrated sulphuric acid to a violet-red solution.

*Nitroperylenequinone*,  $C_{20}H_9O_2 \cdot NO_2$ , forms brownish-red needles and exhibits no sharp melting point. It colours cotton violet and gives a violet-red solution in concentrated sulphuric acid. Its bromo-derivative,  $C_{20}H_8O_2Br \cdot NO_2$ , forms red needles and dyes cotton brown.

T. H. P.

**The Determination of the Relative Strengths of some Nitrogen Bases of the Aromatic Series and of some Alkaloids.** FRANCIS ARNALL (T., 1920, 117, 835-839).

**Preparation of Methyl Derivatives of Arylamino-compounds.** ALPHONSE MAILHE (Brit. Pat. 124219).—Mono- and dimethylated arylamines are obtained by passing a mixture of the vapours of the arylamine and methyl alcohol over a suitable catalyst, preferably precipitated alumina, at a temperature of  $350-400^{\circ}$ , condensing the product, and separating the methylated bases from the condensate. The catalyst is conveniently spread on trays or plates arranged in a series of tubes built into a suitable furnace. The mixture of mono- and di-methylarylamines produced by this process may, if desired, be converted entirely into the dimethylated amine by passing the vapour mixed with a further quantity of methyl alcohol a second time over the catalyst. The exhausted catalyst can be regenerated by calcination in air. Examples are given of the preparation of the mono- and di-methyl-anilines, -toluidines, -xylidines, and -naphthylamines. G. F. M.

**The Sulphonation of *m*-Sulphanilic Acid.** S. C. J. OLIVIER (*Rec. trav. chim.*, 1920, **39**, 499—504).—The author confirms Schultz's view (A., 1906, i, 837) as to the composition of the disulphonic acid obtained by the sulphonation of 3-aminobenzene-1-sulphonic acid by Limpricht and Drebes (*Ber.*, 1876, **9**, 552). When the aminobenzenedisulphonic acid is diazotised in hydrochloric acid solution and then treated with copper, on neutralising the solution with potassium hydroxide, *potassium 2-chlorobenzene-1:4-disulphonate* is obtained, which yields *2-chlorobenzene-1:4-disulphonyl chloride*, m. p. 96·5—97°. This acid chloride, when heated in a sealed tube with phosphorus pentachloride for four hours at 210°, gives 1:2:4-trichlorobenzene, m. p. 17—18°.

W. G.

**Vanillylamine.** E. K. NELSON (U.S. Pat. 1329272).—An alcoholic solution of vanillin is treated with hydroxylamine hydrochloride and sodium carbonate, the excess of alcohol is evaporated after keeping in a warm place for twenty-four hours, and vanillin-oxime is precipitated by water. The oxime in alcoholic solution is reduced by 2·5% sodium amalgam with the gradual addition of glacial acetic acid to maintain an acid reaction. Vanillylamine is then isolated as the hydrochloride.

CHEMICAL ABSTRACTS.

**Some Observations on the "Springing" of "Carbolate" and the Recovery of Phenol from the Resulting Aqueous Layer.** H. M. DAWSON (*J. Soc. Chem. Ind.*, 1920, **39**, 151—152T).—The loss of phenol in the aqueous layer when a solution of sodium phenoxide is neutralised by sulphuric acid is minimised by keeping the volume of the aqueous layer as small as possible, and thereby increasing the salting-out effect of the sodium sulphate. The percentage loss can be calculated from the formula

$$p = 75 \cdot 5 (10^{1 \cdot 92 - 0 \cdot 0036 C_2}) / C_2,$$

where  $C_2$  is the concentration of sodium sulphate (anhydrous) in grams per litre. Experiments were made to recover the phenol from the aqueous layer by extracting with different organic solvents. When 50 grams of the solvent were shaken at 25° with a litre of a solution containing 10 grams of phenol and 200 grams of sodium sulphate, *o*-cresol and *m*-cresol each extracted 75% of the phenol, nitrobenzene 65%, benzene 41%, solvent naphtha (b. p. 145—155°) 40%, and light petroleum (b. p. 95—100°) 4·7%. E. H. R.

**Esterification with Phenols.** M. BAKUNIN and F. GIORDANI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1916, [iii], **22**, 125—134).—The interaction of a phenol and an anhydride serves as a general method for preparing esters in good yields. Various esters have been prepared in this way and their melting points determined by means of Pomilio's apparatus, in which electrical heating is employed.

With quinol and acetic anhydride, the product obtained forms white, micaceous scales, m. p. 119·4°, the reaction being greatly facilitated by the presence of a small proportion of phosphoric oxide, fuming sulphuric acid, or ferric or zinc chloride. These

condensing agents appear to exert, not a dehydrating action, but a catalytic effect, probably of ionic character (compare Bakunin, A., 1916, ii, 421).

The acetyl derivatives of the three nitrophenols are obtained by boiling together the phenol (1 mol.) and acetic anhydride (1 mol.) for ten to fifteen minutes, the presence of fused sodium acetate (compare Noelting, Grandmougin, and Michel, A., 1893, i, 90) being unnecessary. Acetyl-*p*-nitrophenol has m. p.  $78.2^{\circ}$ , and *m*-nitrophenyl acetate,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OAc}$ , crystallises in straw-yellow, shining needles, m. p.  $53.5^{\circ}$ .

The acetyl derivatives of the three hydroxybenzoic acids may be prepared similarly (compare Oddo and Manuelli, A., 1897, i, 180), the melting points being  $137^{\circ}$ ,  $124.1^{\circ}$ , and  $180.5^{\circ}$  for the ortho-, meta-, and para-compounds respectively. Here also phosphoric oxide, fuming sulphuric acid, and zinc chloride act as catalysts, but the actions are not so energetic as with the dihydroxybenzenes and require initial heating.

Phenylcinnamic anhydride,  $(\text{C}_{15}\text{H}_{11}\text{O})_2\text{O}$ , obtained by boiling the acid with phosphoric oxide in chloroform solution (compare Bakunin, *loc. cit.*), forms crystals, m. p.  $120.5^{\circ}$ , and gives rather low values for the molecular weight in freezing benzene, owing possibly to the presence of a little unchanged acid or to dissociation of the anhydride. The phenylcinnamyl derivatives of the three dihydroxybenzenes,  $\text{C}_6\text{H}_4\text{O}_2(\text{C}_{15}\text{H}_{11}\text{O})_2$ , have the melting points  $154.2^{\circ}$ ,  $162.4^{\circ}$ , and  $230^{\circ}$  for the ortho-, meta-, and para-compounds (compare Bakunin, *loc. cit.*) respectively.

T. H. P.

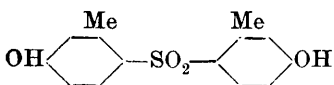
### Preparation of Derivatives of *N*-Acylated *p*-Aminophenols.

FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 318803, additional to D.R.-P. 316902; from *Chem. Zentr.*, 1920, iv, 15).—*N*-Acyl derivatives of the urethanes of *p*-aminophenols are treated with  $\alpha$ -bromodiethylacetyl haloids. The preparation of the bromodiethylacetylurethane of *p*-acetylaminophenol from *p*-acetylaminophenylurethane, m. p.  $181^{\circ}$ , is described. The latter is obtained from guaiacolurethane and *p*-acetylaminophenol by distillation of the guaiacol at  $150^{\circ}$  or by reduction of *p*-nitrophenylurethane, m. p.  $161^{\circ}$ , by hydrogen in the presence of colloidal palladium. *p*-Aminophenylurethane hydrochloride has m. p. about  $235^{\circ}$  after softening above  $200^{\circ}$ , and is acetylated by a mixture of sodium acetate, acetic acid, and acetic anhydride.

H. W.

***m*-Hydroxytolylsulphones.** JOSEF ZEHENTER (*Monatsh.*, 1919, 40, 377—389).—The action of sulphuric acid (about 30%  $\text{SO}_3$ ) on *m*-cresol at  $140^{\circ}$  yields the following two *m*-hydroxytolylsulphones, the  $\beta$ -compound being formed in small proportion.

*$\alpha$* -*m*-Hydroxytolylsulphone (annexed constitution) crystallises in plates or prisms ( $+\frac{1}{2}\text{H}_2\text{O}$ ), m. p.  $115$ — $116^{\circ}$ , and dissolves readily in alkali hydroxides or ammonia, giving solutions from which it is precipitated by addition of acid.



Its *tetrabromo*-derivative,  $C_{14}H_{10}O_4Br_4S$ , forms almost colourless, acicular crystals, m. p.  $225^\circ$ . Its *diacetyl* compound,

$C_{14}H_{12}O_4SAC_2$ , forms prismatic, often crossed, crystals, m. p.  $142^\circ$ , and its *dibenzoyl* derivative,  $C_{14}H_{12}O_4SBz_2$ , groups of radiating, prismatic crystals, m. p.  $153$ — $154^\circ$ . When the sulphone is heated with chromic acid in presence of water, an odour of *p*-benzoquinone is emitted, whilst oxidation with concentrated nitric acid yields 2:4:6-trinitrocresol.

*$\beta$ -m-Hydroxytolylsulphone*, for which various constitutional formulæ are proposed, crystallises with 1MeOH in shining, colourless prisms, m. p.  $196$ — $197^\circ$ , and in a current of air sublimes unchanged at  $180$ — $200^\circ$ . The *diacetyl* derivative,  $C_{14}H_{12}O_4SAC_2$ , forms intergrown, prismatic crystals, m. p.  $197^\circ$ , and the *dibenzoyl* compound,  $C_{14}H_{12}O_4SBz_2$ , microscopic, prismatic crystals, m. p.  $224$ — $225^\circ$ .

Together with these two sulphones, the action of sulphuric acid on *m*-cresol yields 3-cresol-6-sulphonic acid and another cresol-sulphonic acid, probably 3-cresol-2(or 4)-sulphonic acid, the *barium* ( $+ H_2O$ ) and *potassium* ( $+ 2\frac{1}{2}H_2O$ ) salts of which were analysed.

T. H. P.

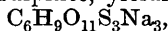
### Compounds of Bivalent Cobalt and Nickel with Catechol.

II. R. F. WEINLAND and ANNA DÖTTINGER (*Zeitsch. anorg. Chem.*, 1920, **111**, 167—174. Compare A., 1918, i, 298).—In an analogous manner to that previously adopted, the authors have prepared a basic sodium salt of cobalto-catechol of the formula  $2[Co(O\cdot C_6H_4O)_2]Na_2\cdot 3NaOH\cdot 14H_2O$ . In the case of nickel, a basic salt was not obtained, but two normal salts,

$[Ni(O\cdot C_6H_4O)_2]Na_2$ ,  $[Ni(O\cdot C_6H_4O)_3]Na_4\cdot 18H_2O$ , in thin, bluish-green leaflets, and  $[Ni(O\cdot C_6H_4O)_2]Na_2\cdot 12H_2O$ , in thick, dark green tablets. A further cobalt derivative of catechol is obtained by heating a solution of cobalt acetate and catechol; this compound crystallises in blue needles, and has the formula  $CH_3\cdot CO_2\cdot Co\cdot O\cdot C_6H_4\cdot OH\cdot H_2O$ . Attempts to prepare a similar nickel derivative failed, but a green powder of the formula  $Ni_3(C_6H_4O_2)_2(OH)_2\cdot 5H_2O$  was obtained.

J. F. S.

**Tautomerism of Phenols. II. Resorcinol.** WALTER FUCHS and BENNO ELSNER (*Ber.*, 1920, **53**, [B], 886—898. Compare this vol., i, 159).—Resorcinol slowly reacts with a boiling aqueous solution of sodium hydrogen sulphite, yielding a substance,



which, in all probability, is the sodium salt of the bisulphite compound of 3:5-diketocyclohexanesulphonic acid, the formation of which can be explained by the assumption that resorcinol reacts in its tautomeric form. It loses a molecule of sulphur dioxide almost instantaneously, even in aqueous solution; a second molecule is eliminated more slowly and with much greater difficulty, whilst the third molecule is only lost to a slight extent even after protracted treatment. When it is allowed to remain for some time

in contact with an aqueous solution of sodium hydroxide at the ordinary temperature, it yields *sodium dihydroresorcinolsulphonate*, colourless needles, which is freely soluble in water and does not give precipitates with the salts of the heavy metals. With ferric chloride, an intense violet-red coloration is developed. It does not show the usual reactions of resorcinol. It is oxidised by potassium permanganate to oxalic acid. It readily absorbs bromine, but simultaneously becomes extensively decomposed, with formation of bromoform. *Dihydroresorcinolsulphonic acid* forms colourless crystals, m. p. 172—175° (decomp.). The *barium* salt is also described. Resorcinol is the main product of the fusion of the latter with potassium hydroxide, whilst also sulphurous acid is removed. The constitution of the sulphonic acid has not been definitely elucidated, but the reaction just described indicates that the sulphonic group is in close proximity to a methylene group, since it is otherwise difficult to explain how a dihydroxylated cyclic sulphonic acid could yield resorcinol with elimination of sulphur dioxide; it appears most probable that the acid has a symmetrical structure.

H. W.

**The Action of an Alcoholic Solution of Potassium Hydroxide in the Presence of Zinc Powder on the Bromobenzhydrols and on some of their Derivatives.** P. J. MONTAGNE (*Rec. trav. chim.*, 1920, **39**, 492—494).—When the bromobenzhydrols or their derivatives are boiled with an alcoholic solution of potassium hydroxide in the presence of zinc powder, the bromine is completely replaced by hydrogen, but little or no resinous material is formed.

W. G.

**Polymorphism of Cholesterol Crystals.** A. RICHAUD (*Compt. rend. Soc. Biol.*, 1920, **83**, 389—391; from *Chem. Zentr.*, 1920, i, 896).—When a solution of cholesterol in hot acetic acid is evaporated, the substance is not infrequently deposited in radiating clusters instead of long needles arranged in crosses; the transformation into rhombic plates by addition of a drop of alcohol does not invariably occur.

H. W.

**Preparation of Metacholesterol.** ISAAC LIFSCHÜTZ (D.R.-P. 318900, 318901; from *Chem. Zentr.*, 1920, iv, 16).—I. Cholesterol or substances containing cholesterol are treated with mild oxidising agents until the formation of oxidation products of cholesterol can just be detected by the acetic-sulphuric acid reaction. *Meta-cholesterol* forms silvery leaflets, m. p. 140—141°; it does not give a coloration with ferric chloride or acetic-sulphuric acid. Its acetyl and benzoyl derivatives also differ from those of cholesterol or oxycholesterol. A solution of metacholesterol in alcohol, after addition of water and removal of alcohol by boiling, gives a perfectly uniform, more or less opalescent, colloidal solution, which can dissolve fats, higher alcohols, etc. Metacholesterol, when melted to the extent of 2% with fats or oils or with vaselin, allows the addition of more than 500% of water.

II. Metacholesterol is obtained from animal matter containing cholesterol (i) by treating the cholesterol substances with solvents according to known processes, whereby the cholesterol is separated in the solid form, and by suitable treatment of the filtrates, preferably by concentration, precipitating metacholesterol, leaving practically only oxysterol in solution; (ii) by treating the mixture with volatile substances and water or with the latter alone, dialysing or filtering the liquid, and fractionating the dissolved matter for the purpose of removing the substances which have smaller power of uniting with water according to (i). Considerable amounts of metacholesterol are contained in ox brain, and more in the blood fat. The great capacity of metacholesterol of mixing with water makes it suitable for the preparation of ointments, cosmetics, emulsions, and similar fatty mixtures with a very high water content. H. W.

**The Polyacid Salts of Monobasic Acids: Sodium Tribenzoate.** PHILIPPE LANDRIEU (*Compt. rend.*, 1920, 170, 1452—1454).—Benzoic acid gives an acid sodium salt having the composition  $C_6H_5 \cdot CO_2Na, 2C_6H_5 \cdot CO_2H$ , which crystallises in silky needles. W. G.

**Hydrogen Persulphides. VI. Trisulphides and Tetrasulphides of certain Carboxylic Acids.** IGNAZ BLOCH and MAX BERGMANN (*Ber.*, 1920, 53, [B], 961—977. Compare A., 1911, i, 46, and previous abstracts).—Acyl disulphides may be readily prepared by the action of the requisite acid chloride on hydrogen disulphide in the presence of a small quantity of zinc chloride. In the case of fatty and fatty-aromatic acid chlorides, the trisulphides may be obtained in a similar manner, but with aromatic acid chlorides there is a marked tendency towards the shortening of the sulphur chain, with the production of disulphides, and this occurs to such an extent as to enable the crude hydrogen polysulphide to be advantageously used in the preparation of the latter. The aromatic trisulphides are readily prepared from sulphur dichloride and the potassium salt of the requisite thioacid ( $2C_6H_5 \cdot CO \cdot SK + SCl_2 = 2KCl + S_3Bz_2$ ), and an extension of this method to sulphur monochloride affords a means of obtaining the tetrasulphides.

The acyl persulphides are, in general, colourless or faintly coloured crystalline substances, which are rather more stable than the hydrogen persulphides, but which, particularly in the cases of the higher sulphides, gradually decompose when preserved. The disulphides have already been extensively investigated; the reactions of the higher sulphides are closely similar to those of the disulphides, the additional sulphur which they contain being generally separated in the elementary state. The tri- and tetrasulphides show a marked tendency to eliminate sulphur and pass into the disulphides, and this action is particularly noticeable in the presence of feebly basic substances, which do not cause too extensive decomposition. Thus benzoyl tetrasulphide could be

degraded step by step by means of dimethylaniline, and benzoyl trisulphide was identified as the primary product of the change.

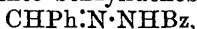
*Acetyl trisulphide*,  $S_3Ac_2$ , forms a greenish-yellow, viscous oil,  $D_4^{20}$  1.3423, which becomes colourless at  $-20^\circ$ , and can be frozen to a crystalline mass, leaflets or needles, m. p.  $-19^\circ$  to  $-17^\circ$ . It could not be prepared in the pure condition. *Phenylacetyl trisulphide*, colourless, six-sided plates, has m. p.  $85-86^\circ$  after slight previous softening, and, with phenylhydrazine yields sulphur, hydrogen sulphide, and the phenylhydrazide of phenylacetic acid, m. p.  $172-173^\circ$ . Phenylacetyl disulphide, prepared from phenylacetyl chloride and hydrogen disulphide, has m. p.  $60-61^\circ$  (compare Johnson, A., 1906, i, 954). *Benzoyl trisulphide* forms prisms, m. p.  $167-168^\circ$  (corr.), but when crystallised from indifferent solvents is obtained in six-sided plates, which soften and partly melt at about  $90^\circ$ , resolidify, and again melt at  $122-123^\circ$  (corr.). The phenomenon appears to depend on polymorphism; conversion of the form of lower into that of higher melting point can be effected by crystallisation from mixtures of chloroform or carbon disulphide and light petroleum in the presence of sulphur charcoal, whilst the reverse change is effected by the use of indifferent solvents. *Benzoyl tetrasulphide* forms almost colourless, flat prisms or broad leaflets, m. p.  $83-84^\circ$ , after very slight previous softening; it is converted by potassium thiobenzoate into benzoyl trisulphide, and, ultimately, benzoyl disulphide. *Anisoyl disulphide*, prepared from potassium thioanisate and oxidising agents or from crude hydrogen persulphide and anisoyl chloride in the presence of zinc chloride, crystallises in needles, m. p.  $121-122^\circ$  (corr.), and resembles benzoyl disulphide closely in its properties (the isolation of *potassium thioanisate* and of *thioanisic acid*,  $OMe \cdot C_6H_4 \cdot CO \cdot SH$ , small, colourless needles, m. p.  $82-83^\circ$ , is described). *Anisoyl tetrasulphide* forms faintly coloured, microscopic needles, m. p.  $104-105^\circ$  (corr.), after slight softening. *Anisoyl trisulphide* closely resembles the benzoyl compound; when crystallised from chloroform in the presence of sulphur chloride, it has m. p.  $168-169^\circ$  (corr.), but, when obtained in the absence of the latter, the melting point is lower and very indefinite, marked softening usually occurring below  $110^\circ$ , and complete liquefaction between  $150^\circ$  and  $160^\circ$ .

H. W.

### The Action of Benzoyl Chloride on Potassium Sulphide.

MAX BERGMANN (*Ber.*, 1920, 53, [B], 979-984).—The action of molar proportions of potassium sulphide and benzoyl chloride in alcoholic solution is stated to lead to the formation of potassium thiobenzoate,  $Ph \cdot COSK$ , which is converted by a second molar proportion of benzoyl chloride into benzoyl sulphide. The reaction is found to follow a much more complex course when the sulphide and chloride are initially present in the molecular ratio, 1:2; benzoyl sulphide is only obtained in small amount, whilst the main products are benzoyl disulphide and a substance which can readily be separated from the latter by reason of its greater stability towards alcoholic ammonia and is regarded as *benzylidene*

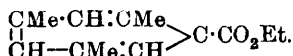
*bisthiobenzoate*,  $\text{CHPh}(\text{S}\cdot\text{COPh})_2$ ; it forms characteristic, moss-like masses of needles or prisms, m. p.  $141^\circ$  (corr.), and is readily decomposed by alcoholic alkali, but is stable to 1% alcoholic hydrogen chloride. The presence of the benzylidene group is proved by its conversion by hydrazine into benzylidenebenzoylhydrazine,



m. p.  $207\text{--}208^\circ$  (corr.). Benzylidene bisthiobenzoate can also be prepared by the action of dry hydrogen chloride on a mixture of benzaldehyde and thiobenzoic acid, or, less advantageously, from benzylidene chloride and potassium thiobenzoate (2 mols.) in alcoholic solution. Benzylidene bisthiobenzoate reacts with piperidine in alcoholic solution to yield *N*-thiobenzoylpiperidine,  $\text{CSPH}\cdot\text{C}_5\text{NH}_{10}$ , pale yellow plates, m. p.  $63\text{--}64^\circ$ , b. p. ca.  $205^\circ/12$  mm. *Anisylidene bisthiobenzoate* forms prisms, m. p.  $79\text{--}80^\circ$ , to a cloudy liquid which becomes transparent at  $81^\circ$ ; it does not appear to yield *N*-thiobenzoylpiperidine with piperidine. H. W.

**Preparation of Chlorylsulphonamides.** MAX CLAASS (D.R.-P. 318899; from *Chem. Zentr.*, 1920, iv, 14—15).—The sulphonamides of aromatic carboxylic acids are converted into the corresponding dichloryl compounds in the usual manner. The introduction of the carbonyl group into the nucleus increases the stability of the chlorylsulphonamides. *Dichlorylsulphonamidobenzoic acid*, from *p*-sulphonamidobenzoic acid and alkali hypochlorite solution and subsequent addition of acetic acid, has m. p.  $203^\circ$ . Sulphuric acid precipitates small amounts of *monochlorylsulphonamidobenzoic acid*, m. p.  $223^\circ$ , from the filtrate. H. W.

**The Action of Diazoacetic Ester on Mesitylene.** EDUARD BUCHNER and KARL SCHOTTENHAMMER (*Ber.*, 1920, 53, [B], 865—873).—Previous investigations (A., 1911, i, 50, and earlier abstracts) have shown that aromatic hydrocarbons condense with ethyl diazoacetate with loss of nitrogen and formation of carboxylic esters of norcarane, and that the latter are transformed at elevated temperatures into derivatives of *cycloheptatriene*. The primary addition appears to occur in such a manner that a quaternary carbon atom is never formed; the case of mesitylene, therefore, is of peculiar interest, since such a grouping must of necessity be present in the initial compound, if actually formed. It is found, however, that the product of the change is *ethyl trimethylcycloheptatrienecarboxylate*, which probably has the constitution



The action between mesitylene and ethyl diazoacetate is best carried out at  $135\text{--}140^\circ$ ; the crude product, when distilled, gives a fraction, b. p.  $137\text{--}143^\circ/12$  mm., which consists of ethyl trimethylcycloheptatrienecarboxylate mixed with ethyl fumarate. At  $115\text{--}120^\circ$ , reaction proceeds very slowly, but ultimately yields the same products; in the presence of copper powder, a brisk action



occurs, which leads almost exclusively to the formation of ethyl fumarate. *Trimethylcycloheptatrienecarboxylic acid*, m. p. 142°, is obtained by hydrolysis of the crude ester mixture, and is converted by the successive action of phosphorus pentachloride and ammonia into the corresponding *amide*, long, colourless needles, m. p. 151°. The acid unites readily with bromine, but the additive product is unstable and easily loses hydrogen bromide.

The first fractions obtained during the distillation of the crude ester give, when hydrolysed, a mixture of trimethylcycloheptatrienecarboxylic acid and mesitylacetic acid, m. p. 168°. The ester of the latter acid is also obtained by the protracted heating of ethyl trimethylcycloheptatrienecarboxylate at 200°, whilst the acid itself is formed when trimethylcycloheptanetricarboxylic acid is treated with glacial acetic acid and hydrogen bromide at the ordinary temperature. The action of bromine on mesitylacetic acid or trimethylcycloheptanetricarboxylic acid in warm glacial acetic acid solution yields *αα-dibromomesitylacetic acid*,  $C_6H_2Me_3 \cdot CBr_2 \cdot CO_2H$ , m. p. 249·5°.

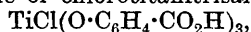
In similar condensations, the formation of derivatives of  $\beta$ -phenylpropionic acid in small quantity has invariably been observed; this appears to be the case in the present instance also, since the action of alcoholic ammonia on the ester very slowly leads to the formation of mesitylacetamide and an *amide*, m. p. 118°, which, when hydrolysed, yields an *acid*, m. p. 46·5°, probably  $\beta$ -3:5-dimethylphenylpropionic acid; it could not be obtained in quantity sufficient for an extended investigation.

Trimethylcycloheptanetricarboxylic acid absorbs six atoms of hydrogen in glacial acetic acid solution in the presence of platinum and gives the oily *trimethylcycloheptanetricarboxylic acid*, which is stable towards permanganate, and is characterised by conversion into the corresponding *amide*, long needles, m. p. 148°. H. W.

**Melting Point of Salicylic Acid.** W. J. BUSH & Co., LTD. (*Perfumery and Essent. Oil Rec.*, 1920, **11**, 207).—Pure salicylic acid melts at 159°, and m. p. of 158° to 159° are regularly obtained with commercial samples of British salicylic acid. The m. p. 156—157°, quoted in the pharmacopœia and commonly accepted, is consequently considerably too low. G. F. M.

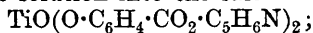
**Molecular Compounds of Inorganic Haloids. VII. Hydroxycarboxylic Acid Titanates, Polyphenol Titanates, and certain Allied Compounds.** ARTHUR ROSENHEIM and OTTOKAR SORGE (*Ber.*, 1920, **53**, [B], 932—939).—A further extension of previous work (compare A., 1915, i, 537, and previous abstracts).

*Titanitrisalicylic acid*,  $C_6H_4 \begin{smallmatrix} \diagup O \diagdown \\ CO_2 \end{smallmatrix} Ti(O \cdot C_6H_4 \cdot CO_2H)_2$ , is obtained when the hydrochloride of chlorotitanitrisalicylic acid,



is exposed to the air; the *pyridinium*, *ammonium*, *sodium*, and *potassium* salts are described.

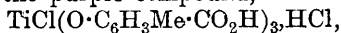
Titanidisalicylate,  $\text{Ti}\left(\begin{smallmatrix} \text{O} \cdot \text{C}_6\text{H}_4 \\ \text{O} \cdot \text{CO} \end{smallmatrix}\right)_2$  (*loc. cit.*), is converted by pyridine in alcoholic solution into the salt



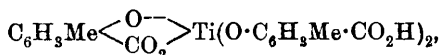
the corresponding *ammonium* and *mercuric* salts have been investigated.

Titanium chloride reacts with a solution of phenyl salicylate in anhydrous ether to yield the compound  $[\text{Ti}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Ph})_3]_2\text{TiCl}_6$ ; with salicylamide, under the same conditions, a brown, smeary mass is obtained, which evolves hydrogen chloride and gives  $[\text{TiCl}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2)_3]_3\text{HCl}$ ; an alcoholic solution of the latter deposits the compound  $\text{TiCl}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2)_3 \cdot \text{EtOH}$ .

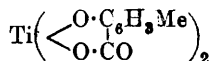
The behaviour of *m*-cresotic acid closely resembles that of salicylic acid. Thus, the purple compound,



passes, on exposure to air, into the yellowish-white acid,



the *pyridinium* and *ammonium* salts of which are described. The acid is converted by heat into titanium basic *m*-cresotate,



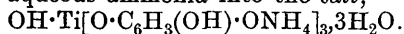
which is transformed by alcohol and pyridine into the yellow salt,  $\text{TiO}(\text{O} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO}_2 \cdot \text{C}_5\text{H}_6\text{N})_2$ ; the corresponding *ammonium* and *potassium* salts are described.

Other hydroxycarboxylic acids appear to react in an analogous manner with titanium chloride; the salts derived from protocatechuic, gallic, and pyrogallolcarboxylic acids were, however, too soluble to permit their isolation in the pure state.

In the compounds which have been described so far, the hydroxyl group is, from the point of view of the co-ordination theory, equivalent to the carboxyl group. It is, therefore, not surprising to find that the polyphenols yield complexes with titanium tetrachloride. Thus, when ethereal solutions of catechol and titanium chloride are mixed, a vigorous action occurs, the primary product of which could not be isolated; if, however, the ether is removed and the residue treated with aqueous ammonia, the *ammonium* salt,

$\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} \right\rangle \text{Ti}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{ONH}_4)_2 \cdot \text{H}_2\text{O}$ , is obtained (the corresponding *potassium* and *silver* salts are described). Other chlorides behave similarly. Thus, silicon tetrachloride and catechol give colourless, very unstable crystals of *tricatechol silicon chloride* (?), which are converted by alcoholic ammonia into *ammonium triccatechol silicate*,  $\text{C}_6\text{H}_4\text{O}_2 \cdot \text{Si}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{ONH}_4)_2$ , and by alcoholic pyridine into the corresponding *pyridinium* salt. Similarly, zirconium oxychloride and thorium nitrate react with a boiling aqueous ammoniacal solution of catechol to yield the salts,  $\text{C}_6\text{H}_4\text{O}_2 \cdot \text{Zr}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{ONH}_4)_2 \cdot 7\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_4\text{O}_2 \cdot \text{Th}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{ONH}_4)_2 \cdot 7\text{H}_2\text{O}$ .

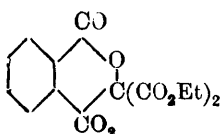
Titanium chloride reacts readily with pyrogallol in ethereal solution, and the product obtained after removal of the solvent is transformed by aqueous ammonia into the salt,



H. W.

**The Constitution of Phthalylmalonic Esters and Allied Substances.** JOHANNES SCHEIBER and GEORG HOPFER (*Ber.*, 1920, **53**, [B], 898—913).—Recent spectrochemical observations (A., 1918, i, 436) have led Auwers and Auffenberg to cast doubts on the correctness of the formula,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CO} \\ \text{CO}\end{smallmatrix}\rangle\text{C}(\text{CO}_2\text{Et})_2$  (I), assigned to phthalylmalonic ester by Scheiber (A., 1912, i, 559), and to revert to the older formula,  $\text{CO}\langle\begin{smallmatrix}\text{C}_6\text{H}_4 \\ \text{O}\end{smallmatrix}\rangle\text{C}:\text{C}(\text{CO}_2\text{Et})_2$  (II). The problem has now been re-investigated by examining the action of ozone on the ester and a number of related compounds.

A substance of formula (II) would be expected to react with ozone to give an ozonide which would be decomposed by cold water with the formation of phthalic acid and ethyl mesoxalate; the accumulation of negative substituents around the double bond would not inhibit this reaction, since it is found that the similarly constituted benzylidenephthalide yields phthalic acid and benzaldehyde, whilst benzylidenemalonic acid gives benzaldehyde or benzoic acid and mesoxalic acid, and  $\alpha$ -cyanocinnamic ester yields benzaldehyde or benzoic acid and the semi-nitrile of mesoxalic ester (*phenylhydrazone*, silky leaflets, m. p.  $181^\circ$ ). Actually, ethyl phthalylmalonate is only slowly attacked by ozone at  $-20^\circ$  and yields small amounts of phthalic acid and ethyl mesoxalate, but the main product (about 80%) is an oily substance (this occasionally solidifies to a colourless mass, m. p. about  $48^\circ$ , which cannot be further purified), which is characterised by its unusual stability towards water and appears to be a peroxide, probably having the



annexed formula. Hydrolysis of the latter, in so far as it can be effected by water, leads to the production of phthalic acid and ethyl mesoxalate, and this doubtless accounts for a portion of these substances which are found after ozonisation of phthalylmalonic ester.

The results of the experiments, therefore, tend to confirm the symmetrical structure of the ester, and the apparent discordance between the authors' conclusions and those of Auwers and Auffenberg are ascribed to the dissimilarity of the experimental conditions and to the possibility of desmotropic change. It appears that the solid ester has the constitution (I), and, in the molten or dissolved state, passes more or less completely into the forms (II) or (III),  $\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}(\text{CO}_2\text{Et})_2$ ; indications of the presence of the latter are yielded by the evolution of carbon dioxide during ozonisation.

Very similar observations are recorded with succinylmalonic ester, which, after ozonisation and treatment of the product with water, is found to give small quantities of succinic acid and ethyl mesoxalate, the main product, however, being a *diperoxide* characterised by great stability towards water. The solid ester, therefore, appears to have the symmetrical constitution and to undergo desmotropic change when melted or dissolved.

When similarly treated, the two ethyl phthalylacetoacetates yield phthalic acid, acetic acid, and ethyl glyoxylate, but whereas the ester of lower melting point gives the products in quantitative amount, that of higher melting point only gives them in 60% yield. The constitution of the former is without doubt expressed by the formula  $\text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}(\text{CO}_2\text{Et})_2$ , whilst the latter in all probability has

the constitution  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{CO} \end{smallmatrix} \text{C} \begin{smallmatrix} \diagup \text{COEt} \\ \diagdown \text{COMe} \end{smallmatrix}$ ; in any case, the structure  $\text{CO} \begin{smallmatrix} \diagup \text{C}_6\text{H}_4 \\ \diagdown \text{O} \end{smallmatrix} \text{C} \begin{smallmatrix} \diagup \text{COMe} \\ \diagdown \text{CO}_2\text{Et} \end{smallmatrix}$  is definitely excluded, since such a compound would yield phthalic acid and ethyl  $\alpha\beta$ -diketobutyrate, the latter of which is not produced.

The results of ozonisation do not completely confirm the constitutions previously ascribed to the phthalylbenzoylacetones; the smooth conversion of the isomeride of lower melting point into phthalic acid and phenyl methyl triketone indicates that it has the formula  $\text{CO} \begin{smallmatrix} \diagup \text{C}_6\text{H}_4 \\ \diagdown \text{O} \end{smallmatrix} \text{C} \begin{smallmatrix} \diagup \text{COMe} \\ \diagdown \text{COPh} \end{smallmatrix}$ . The constitution of the isomeride of higher melting point has not been definitely elucidated, but the present investigation accentuates the improbability that the compounds are stereoisomerides.

Phthalylacetylacetone yields phthalic acid, methylglyoxal, and acetic acid, thus confirming the structure,  $\text{CC} \begin{smallmatrix} \diagup \text{C}_6\text{H}_4 \cdot \text{CO} \\ \diagdown \text{O} - \text{CMe} \end{smallmatrix} \text{C} \cdot \text{COMe}$ , assigned to it previously.

H. W.

[**Formation of Iron Tannates.**] C. A. MITCHELL (*Analyst*, 1920, **45**, 254—256).—When solutions of ferrous salts and gallo-tannic acid are mixed, a pale ferrous tannate appears to be formed, any ferric salt present being immediately reduced to the ferrous condition. When this solution of ferrous tannate is exposed to the air, it is slowly oxidised, and yields insoluble incrustations and deposits. The earlier precipitates contain a proportion of iron (for example 5.38—5.75%) corresponding with Wittstein's iron tannate,  $\text{Fe}_2(\text{C}_{14}\text{H}_9\text{O}_9)_6$  (*Jahresber. Chem.*, 1848, **28**, 221). As the oxidation proceeds, the successive deposits contain more iron, and finally approximate in composition to the precipitate which Pelouze (*Ann. Chim. Phys.*, 1833, [ii], **54**, 337) obtained by exposing a solution of ferric sulphate and gallotannic acid to the air for a month, namely,  $\text{C}_{14}\text{H}_8\text{O}_9 \gg \text{Fe} \cdot \text{Fe} \ll \text{C}_{14}\text{H}_8\text{O}_9$ , which contains 8.4% of iron. This compound, however, is not formed at

first from ferric sulphate, but the presence of ferric salts in the solution promotes the oxidation to the more highly oxidised compounds. The addition of a small amount of hydrogen peroxide to a solution of ferrous tannate causes the precipitation of a tannate containing iron, corresponding with the amount (14.21%) in Wittstein's tannate,  $\text{C}_{14}\text{H}_9\text{O}_9 \begin{smallmatrix} \text{O} \\ \text{>} \end{smallmatrix} \text{Fe} \cdot \text{Fe} \begin{smallmatrix} \text{O} \\ \text{<} \end{smallmatrix} \text{C}_{14}\text{H}_9\text{O}_9$ . If a large amount of hydrogen peroxide is added, a heavy precipitate containing 21 to 24% of iron is immediately formed. This approximates in composition to Ruoss's basic tannate,  $(\text{C}_{14}\text{H}_7\text{O}_9)(\text{FeO})_2$ , with 24.42% of iron (*Zeitsch. anal. Chem.*, 1902, **41**, 732). Neither of these compounds, however, appears to be formed in the atmospheric oxidation of ferrous tannate. By adding a few drops of pine oil to a ferrous tannate solution, a dense precipitate containing about 8.1% of iron is obtained. A similar catalytic acceleration of the oxidation to Pelouze's tannate is effected by the addition of saliva, but in this case the action proceeds much more slowly.

C. A. M.

#### Manufacture of Hydroxyaldehydes and their Ethers.

ANDRE WEISS (Brit. Pat. 139153).—Aromatic hydroxyaldehydes or their ethers are obtained by the interaction of a phenol or phenol ether with formaldehyde and an aromatic nitroso-compound, such as nitrosobenzene, *p*-nitrosodimethylaniline, etc. For example, vanillin is obtained in excellent yield by heating for several hours on a water-bath a mixture of guaiacol (1 mol.), formaldehyde (1 mol.), and *p*-nitrosodimethylaniline ( $\frac{1}{2}$  mol.), methyl or ethyl alcohol being added as a diluent, and hydrogen chloride being bubbled through continuously. *p*-Aminodimethylaniline is formed as a by-product, and is removed by extraction with benzene or ether after rendering alkaline with sodium hydroxide and distilling off the alcohol. The liquor is then acidified and the vanillin extracted with benzene and purified by distillation in a vacuum.

G. F. M.

**Influence of Substitution in the Components on the Equilibria in Binary Solutions. XXVI. The Binary Systems of Acetophenone and Benzophenone, respectively, with Phenols and their Derivatives.** ROBERT KREMANN and HERMANN MARKTL (*Monatsh.*, 1920, **41**, 43—75. Compare this vol., i, 564).—Freezing-point curves have been constructed for the binary systems, acetophenone with  $\alpha$ -naphthol,  $\beta$ -naphthol, catechol, quinol, resorcinol, pyrogallol, phenol, *o*-nitrophenol, *m*-nitrophenol, *p*-nitrophenol, 2:4-dinitrophenol, and picric acid respectively, and for benzophenone with picric acid and 2:4-dinitrophenol. It is shown that both  $\alpha$ -naphthol and  $\beta$ -naphthol form an equimolecular compound with acetophenone, melting at 13° and 8° respectively. The three dihydroxybenzenes each form an equimolecular compound with acetophenone, which melts as follows: quinol, 40°; resorcinol, 13°; catechol, 1°. Pyrogallol forms two compounds with acetophenone, one molecule of aceto-

phenone combining with one half and one molecule of pyrogallol respectively, and the compounds melting at  $18.5^{\circ}$  and  $21^{\circ}$ . It is shown that the equimolecular compound with catechol is very much more dissociated in the fused mass than that with resorcinol. Benzophenone forms no compounds with any of the substances used; here simple eutectics are formed, as follows: at  $35^{\circ}$ , with 20% of 2:4-dinitrophenol, and at  $27^{\circ}$  with 29% of picric acid. Acetophenone forms no compounds with the nitrophenols or with 2:4-dinitrophenol; here, again, simple eutectics are formed as follows: at  $2.5^{\circ}$ , with 47% of *o*-nitrophenol; at  $-16^{\circ}$ , with 41.5% of *m*-nitrophenol; at  $-4^{\circ}$ , with 38% of *p*-nitrophenol; at  $12^{\circ}$ , with 21% of 2:4-dinitrophenol. In the case of picric acid, an equimolecular compound between acetophenone and picric acid, and a further compound between two molecules of acetophenone and one molecule of picric acid, m. p.  $50^{\circ}$ , are formed. J. F. S.

**Asymmetric Synthesis.** RICHARD WEISS (*Monatsh.*, 1919, **40**, 391—402).—The interaction of phenyl-*p*-tolylketen and *l*-menthol in absolute ethereal solution yields *l*-menthyl *d*-phenyl-*p*-tolylacetate. This reaction represents an asymmetric synthesis, since an optically active compound is formed from an optically inactive one without the intermediate formation of the racemic compound. According to the author's results, the *l*-menthyl *d*-phenyl-*p*-tolylacetate described by McKenzie and Widdows (*T.*, 1905, **107**, 702) was partly racemised.

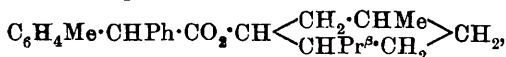
*Dibromobenzyl p-tolyl ketone*,  $\text{CBr}_2\text{Ph}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}$ , crystallises in yellow prisms, m. p.  $127.5$ — $128^{\circ}$ , and yields *p*-toluic acid when fused with potassium hydroxide. When heated with alcohol in a sealed tube at  $140$ — $160^{\circ}$ , it gives:

*4-Methylbenzil*,  $\text{COPh}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}$ , which forms crystals, m. p.  $99$ — $101^{\circ}$ , and distils unchanged in a vacuum. Since the action of hydrazine on an alcoholic solution of 4-methylbenzil yields only a small proportion of a crystalline substance, together with much syrupy material incapable of purification, the preparation of the phenyl-*p*-tolylketen was carried out by way of phenyl-*p*-tolylglycollic acid.

*Phenyl-p-tolylglycollic acid*,  $\text{OH}\cdot\text{CPh}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CO}_2\text{H}$ , prepared by heating 4-methylbenzil with potassium hydroxide solution at  $150$ — $160^{\circ}$ , forms crystals, m. p.  $131$ — $133^{\circ}$ , and is coloured blood-red by concentrated sulphuric acid.

*$\alpha$ -Chlorophenyl-*p*-tolylacetyl chloride*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CPhCl}\cdot\text{COCl}$ , prepared by the method used by Staudinger for  $\alpha$ -chlorodiphenylacetyl chloride (*Annalen*, 1907, **356**, 72), forms a yellow oil, which is decomposed with moderate rapidity by atmospheric moisture.

*l*-Menthyl *d*-phenyl-*p*-tolylacetate,



prepared by reducing  $\alpha$ -chlorophenyl-*p*-tolylacetyl chloride with zinc turnings under ether and in an atmosphere of carbon dioxide, and treating the phenyl-*p*-tolylketen thus formed with *l*-menthol,

forms a yellow, viscous oil, b. p. 190—196°/1 mm.,  $[\alpha]_D$  in acetone  $-45.40^\circ$ . The ester is accompanied by a small proportion of phenyl-*p*-tolylacetic acid, due to the action of water on the keten.

The phenylacetic acid used for the synthesis of the benzyl *p*-tolyl ketone was prepared by converting benzyl chloride into benzyl cyanide and hydrolysing the latter, and was found to be mixed with a little *phenylacetobenzylamide*,  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$ , which may also be obtained by the Schotten-Baumann reaction from benzylamine and phenylacetyl chloride, and forms crystals, m. p. 122°. This compound is formed in accordance with the following scheme:  $\text{CH}_2\text{Ph}\cdot\text{CN} + \text{CH}_2\text{PhCl} \rightarrow \text{CH}_2\text{Ph}\cdot\text{CCl}\cdot\text{N}\cdot\text{CH}_2\text{Ph} \rightarrow \text{CH}_2\text{Ph}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{CH}_2\text{Ph} \rightarrow \text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$ .

T. H. P.

**The Action of an Alcoholic Solution of Potassium Hydroxide in the Presence of Zinc Powder on the Bromobenzophenones and on some of their Derivatives.** P. J. MONTAGNE (*Rec. trav. chim.*, 1920, **39**, 483—491).—Bromobenzophenones and their derivatives when boiled in an alcoholic solution of potassium hydroxide with zinc powder are reduced to benzhydrols, but, at the same time, the bromine is completely replaced by hydrogen, and a certain amount of resinous material is formed.

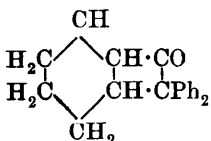
W. G.

**Ketens. XXXI. *cyclo*Butanedione Derivatives and the Polymeric Ketens.** H. STAUDINGER (*Ber.*, 1920, **53**, [B], 1085—1092).—It has recently been suggested by Schroeter (A., 1917, i, 145) that the polymeric ketens are molecular compounds instead of *cyclobutane* derivatives, as postulated by Staudinger. The author does not agree with this view, and, in the present communication, gives a survey of the literature of this class of substances, in which it is shown that their properties can be adequately interpreted by the *cyclobutane* formulation. New experimental evidence is not brought forward.

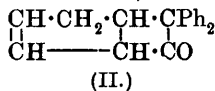
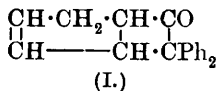
H. W.

**Ketens. XXXII. *cyclo*Butane Derivatives from Diphenylketen and Ethylene Compounds.** H. STAUDINGER and E. SUTER [and, in part, R. FLATT, H. W. KLEVER, KARL KNOCH, and E. STANDT] (*Ber.*, 1920, **53**, [B], 1092—1105).—Diphenylketen readily condenses with styrene, yielding 1:1:3-*triphenylcyclobutane-2-one*,  $\text{CHPh}\cdot\text{CH}_2\cdot\text{OC}\cdot\text{CPh}_2$ , colourless needles, m. p. 135—136°, from which the initial products are regenerated by heating at about 200°. The substance could not be caused to yield an oxime, semicarbazone, or phenylhydrazone, nor did it condense with benzaldehyde in the presence of alkali. When treated with methyl-alcoholic sodium hydroxide solution, it gives *αα*-*triphenyl-n-butylric acid*, white powder, m. p. 178—179° (*methyl ester*, m. p. 125—126°), which is converted at 260° into styrene and diphenylacetic acid. Similarly, diphenylketen and *p*-methylstyrene give 1:1-*diphenyl-3-p-tolylcyclobutane-2-one*, colourless needles, m. p. 117°, which is decomposed into its constituents by heat, and with alkali gives

*αα*-diphenyl-γ-p-tolyl-n-butyric acid, white powder, m. p. 207°. *p*-Chlorostyrene, b. p. ca. 74°/12 mm., is prepared by the action of magnesium methyl iodide on *p*-chlorobenzaldehyde and subsequent dehydration of the carbinol so formed by heating it with potassium pyrosulphate; the yields are poor (30%), on account of the readiness with which polymerisation occurs. With diphenylketen, the substance yields 1:1-diphenyl-3-*p*-chlorophenylcyclobutane-2-one, crystalline powder, m. p. 120—121°, from which *αα*-diphenyl-γ-*p*-chlorophenyl-n-butyric acid, m. p. 178—179°, is obtained in the usual manner. Similarly, 1:1-diphenyl-3-*p*-anisylcyclobutane-2-one, m. p. 77—78°, is prepared from *p*-methoxystyrene. Vinyl ethyl ether unites with diphenylketen to form 1:1-diphenyl-3-ethoxycyclobutane-2-one, crystalline powder, m. p. 71—72°, which is relatively unstable and decomposes into its constituents when gently heated, and, apparently,



when preserved; it is converted by alcoholic alkali into an acid, m. p. about 116°. Tetrahydrobenzene and diphenylketen yield a substance (annexed formula), colourless needles, m. p. 129—130°, which is transformed by alkali into diphenylcyclohexylacetic acid, crystalline powder, m. p. 122°. cyclopentadiene and diphenylketen unite readily in molar proportions, giving the compound I or II, m. p. 89—90°, which is readily resolved by heat into



its components, and with alkali gives the corresponding acid, m. p. 125°. The substance is readily reduced to the corresponding saturated compound, colourless needles, m. p. 92°, which decomposes when heated into diphenylketen and cyclopentene. Diphenylketen unites similarly with phenylmethylfulvene to yield a product, m. p. 168—169°. Unlike the previous cases, *N*-methylpyrrole unites with two molecules of diphenylketen even when the substances are used in molar proportions; the product is a white, crystalline powder, m. p. ca. 200° (decomp.) after softening at 190°. Pyrrole itself yields *N*-diphenylacetylpyrrole, m. p. 122°. *as*-Diphenylethylene gives 1:1:3:3:5:5-hexaphenylcyclohexane-2:4-dione, m. p. 180—181°, which yields *ααγγεε*-hexaphenyl-δ-ketohexoic acid, needles, m. p. 121—123°. H. W.

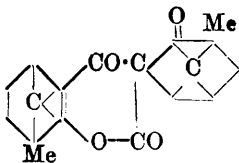
### Ketens. XXXIII. Attempts to Prepare Optically Active

**Ketens.** H. STAUDINGER and S. SCHOTZ (*Ber.*, 1920, 53, [B], 1105—1124).—The investigation was undertaken in the hope that the isolation of an optically active keten would greatly facilitate the investigation of the rate at which these substances unite with various compounds by allowing the course of the reaction to be followed polarimetrically. The present communication describes the efforts to obtain certain camphorketens. Unfortunately, the

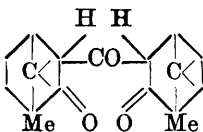


substances are too unstable to permit their isolation in the unimolecular form, but various dimerides have been obtained and characterised as *cyclobutane* derivatives. The fact that in certain instances stereoisomerides can be isolated is further evidence against Schroeter's conception of the substances as additive products.

Camphorcarboxylic chloride is most conveniently prepared by the action of thionyl chloride at the ordinary temperature on the corresponding acid. When heated, it loses hydrogen chloride rapidly at 170°, slowly, but with the production of a purer product, at 100°, and passes into the pyronone derivative (annexed formula), needles, m. p. 196°,  $[\alpha]_D + 293.8^\circ$  in benzene,  $+ 302.2^\circ$  in ethyl acetate solution, which is identical with the product obtained by

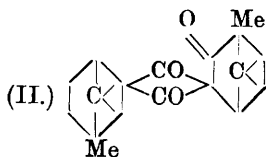
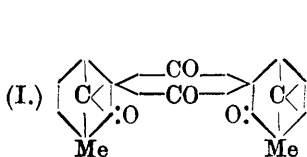


Kachler and Spitzer by the action of acetyl chloride on camphorcarboxylic acid. Attempts to depolymerise the substance were unsuccessful. When subjected to the prolonged action of concentrated hydrochloric acid at the ordinary temperature, the dimeride is transformed into the corresponding hydroxy-acid, m. p. 262° (Kachler and Spitzer give m. p. 264°), which, when heated at about 290°/0.1 mm., is reconverted into the substance, m. p. 196°, a little camphor being simultaneously formed. The acid is very sensitive towards alkali, and is converted by aqueous potassium hydroxide into the *ketone* (annexed formula), m. p. 180°.



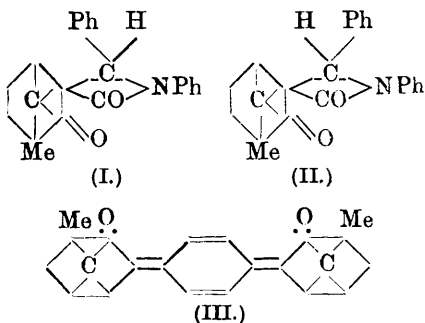
Attempts were made to prepare camphorketen from bromocamphorcarboxyl bromide (the latter, m. p. 80–81°, is obtained by the action of bromine in the presence of carbon disulphide on camphorcarboxyl chloride, removal of the halogen acids from the solution by carbon dioxide, and subsequent treatment of the solution with hydrogen bromide); the bromide reacts readily with zinc in ethereal solution, but yields only the acid, m. p. 264°, and the pyronone compound, m. p. 196° (see above).

Camphorcarboxyl chloride readily loses hydrogen chloride under the influence of basic reagents, particularly quinoline, and the resultant solution contains *camphorketen* in the free state for a short period. Polymerisation, however, readily results, with the formation of a mixture of *cis*- and *trans*-*dicamphorcyclobutanediones* (I and II); the former has m. p. 152–153°,  $[\alpha]_D + 116.3^\circ$  in benzene,



$+ 126.8^\circ$  in ethyl acetate solution, whilst the latter has m. p. 150–151°,  $[\alpha]_D + 61.1^\circ$  in benzene,  $+ 62.9^\circ$  in ethyl acetate. When

either polymeride is heated for a short time at 160—170°, the keten is transitorily formed, which rapidly passes into the pure product of m. p. 196°. With *p*-toluidine, either substance gives camphor-carboxyl-*p*-toluidide, whilst with hydrochloric acid the same acid is obtained as from the pyronone derivative; with methyl alcohol and alkali, *methyl camphorcarboxylate*, b. p. 143—145°/12 mm., 142°/13 mm.,  $[\alpha]_D +57.91^\circ$  in ethyl acetate solution, is obtained. With ethyl-alcoholic potassium hydroxide solution, the reaction follows a different course, yielding small amounts of a new *acid*, m. p. about 187°, but neither camphorcarboxylic acid nor its ethyl ether; the main product is dicamphorketone, m. p. 182° (see above),



which is more conveniently prepared by the action of dilute aqueous sodium hydroxide on an ethereal solution of either polymeride.

The formation of camphorketen from the *cyclobutanedione* derivative is established, not only by the appearance of coloration, but also by addition of certain reagents, which combine so rapidly with the keten that combination

occurs before polymerisation can take place. Thus, for example, the dicamphor*cyclobutanediones* readily react with benzylideneaniline to yield the two stereoisomeric  $\beta$ -lactams (I and II), m. p.'s 166.5° and 195—196° respectively, and with *p*-benzoquinone to give *dicamphorquinodimethane* (III), orange-coloured crystals, m. p. 305—306°.

H. W.

**The Chloroquinones.** A. J. DEN HOLLANDER (*Rec. trav. chim.*, 1920, **39**, 481—482).—The author has repeated the work of Peratoner and Genco (A., 1895, i, 342) and of Oliveri Tortorici (A., 1898, i, 303) on the preparation of 2:3-dichloro-*p*-benzoquinone. He found no evidence of the formation of this compound, the products he obtained being 2:5-dichloro-*p*-benzoquinone and 2:6-dichloro-*p*-benzoquinone.

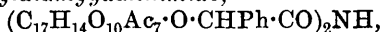
W. G.

**The Fission of certain Glucosides and Amygdalin.** GÉZA ZEMPLÉN (*Ber.*, 1920, **53**, [B], 996—1006).—Amygdalin is known to contain a biose which is hydrolysed by acids or by emulsin to two molecules of dextrose, but its identity has not been further established. The experiments now described were undertaken in the hope that hepta-acetylamygdalin might undergo fission under the influence of a solution of hydrogen bromide in glacial acetic acid in such a manner as to yield phenylbromoacetonitrile and the acetyl bromo-compound of the biose of amygdalin. The feasibility of this plan is shown by experiments with a number of acetylated

cellobiosides, but, unfortunately, the process proves not to be available for amygdalin, in which the presence of the cyanogen group renders the glucosidic union between mandelic acid and the biose more stable than the ethereal bond between the two glucose residues. Attempts to avoid this difficulty by using hepta-acetyl-amygdalinic acid were unsuccessful, and it was further not found possible to obtain a suitable crystalline derivative of amygdalin which was free from nitrogen.

*Hepta-acetylbenzylcellobioside*,  $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{C}_{12}\text{H}_{14}\text{O}_{10}\text{Ac}_7$ , long, colourless, silky needles, m. p.  $193^\circ$  after softening at  $190^\circ$ ,  $[\alpha]_D^{20} - 37.4^\circ$  in chloroform solution, is prepared by the interaction of acetylbromocellobiose and benzyl alcohol in benzene solution in the presence of silver carbonate, and is hydrolysed by hydrogen bromide in glacial acetic acid to acetylbromocellobiose, m. p. about  $190^\circ$  (decomp.),  $[\alpha]_D^{20} + 92.0^\circ$  in chloroform solution. Under similar conditions, the latter substance was also obtained from *hepta-acetylmethylcellobioside*, small, colourless needles, m. p.  $180^\circ$ , from *hepta-acetylisobutylcellobioside*, slender, colourless needles, m. p.  $196-197^\circ$ ,  $[\alpha]_D^{12} - 21.5^\circ$  in chloroform solution, and from *hepta-acetylphenylcellobioside*, yellowish-grey needles, m. p.  $193^\circ$  (prepared from phenol and acetylbromocellobiose in the presence of quinoline). Tetra-acetyl- $\beta$ -methylglucoside appeared to undergo fission in a similar manner, since, although acetylbromoglucose could not be isolated in the crystalline state, its presence could be deduced from the abundant formation of phenylglucosazone after hydrolysis of the product with calcium carbonate and subsequently with aqueous alcoholic alkali. On the other hand, tetra-acetylsalicin yielded *tetra-acetylsalicin bromide*,  $\text{CH}_2\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_7\text{O}_5\text{Ac}_4$ , long, colourless prisms, m. p.  $167^\circ$ ,  $[\alpha]_D^{15} + 47.1^\circ$  in chloroform solution, the free hydroxyl groups of the saligenin residue being replaced by bromine.

*Tetradeca-acetyldiamygdalinimide*,



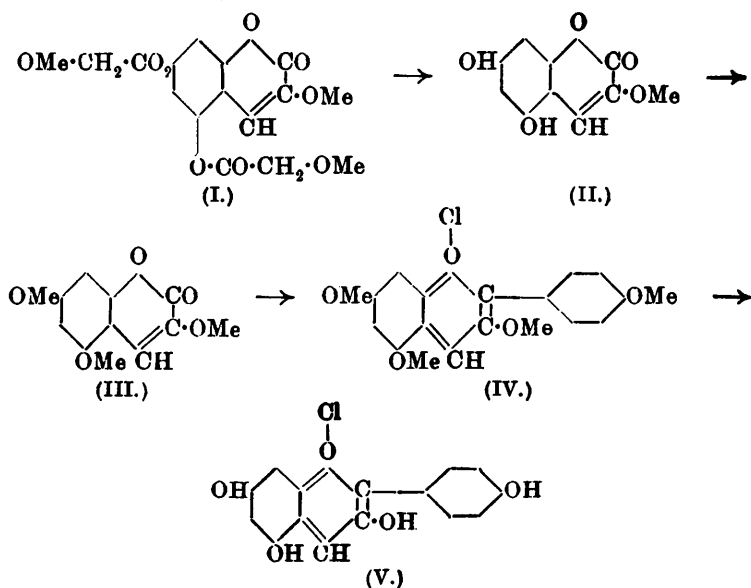
is prepared by saturating a solution of hepta-acetylamygdalin in chloroform containing a little absolute alcohol with dry hydrogen chloride; it forms long needles, m. p.  $212^\circ$ ,  $[\alpha]_D^{21} - 72.1^\circ$  in chloroform solution. It is hydrolysed by alcoholic potassium hydroxide solution to *diamygdalinimide*, which is hydrolysed by boiling aqueous hydrochloric acid with abundant production of dextrose.

H. W.

**Action of Light on Colloidal Chlorophyll in the Presence of Stabilising Agents.** RENÉ WURMSER (*Compt. rend. Soc. Biol.*, 1920, **83**, 437-438; from *Chem. Zentr.*, 1920, i, 895).—Colloidal chlorophyll, prepared according to the directions of Willstätter and Stoll, is much more sensitive to light than the natural product. This sensitiveness can be greatly depressed by certain colloids, of which gelatin appears to be the most potent; white of egg and gum arabic are much less powerful, whilst starch is inactive. Possibly an action of salts on the complex may be observed in plants. If the effect of the protective colloid is due to shielding

from oxygen, the same effect may possibly be expected from carbon dioxide. H. W.

**Synthesis of Pelargonidine.** RICHARD WILLSTÄTTER and LÁSZLÓ ZECHMEISTER (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1914, **34**, 886—893).—The condensation of 2:4:6-trihydroxybenzaldehyde with sodium methoxyacetate and methoxyacetic anhydride at 150—155° gives 5:7-dimethoxyacetyl-3-methoxycoumarin (I), prisms, m. p. 170—171° (corr.), from which, by treatment with cold dilute sodium hydroxide solution, 5:7-dihydroxy-3-methoxycoumarin (II), prisms or rhombic leaflets, m. p. 280—285° (corr.; decomp.), is obtained. 3:5:7-Trimethoxycoumarin (III), prisms or oblong leaflets, m. p. 171—172° (corr.), formed from the latter by treatment with diazomethane, reacts with excess of magnesium anisyl bromide, the product giving 3:5:7-trimethoxy-2-p-anisylpyrylium chloride (IV), bluish-red prisms (compare Decker and Fellenberg, A., 1907, i, 1064), from which the methyl groups are removed by means of boiling hydriodic acid in presence of phenol. 3:5:7-Trihydroxy-2-p-hydroxyphenylpyrylium iodide thus obtained gives a corresponding chloride (V), identical in composition, crystalline form, solubility, reaction, and absorption spectrum with the chloride of natural pelargonidine (Willstätter and Bolton, A., 1914, i, 564; 1915, i, 283).

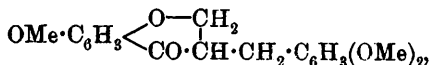


J. K.

**Chromanones. II. The Brazilin and Hæmatoxylin Question.** P. PFEIFFER and H. J. EMMER (*Ber.*, 1920, **53**, [B], 945—953).—A further contribution to the synthesis of substances

allied to brazilin and hæmatoxylin (compare Pfeiffer and Grimmer, A., 1917, i, 661).

**7-Methoxychromanone** [7-methoxy-2:3-dihydro- $\gamma$ -benzopyrone] condenses with vanillin methyl ether in alcoholic solution in the presence of sodium hydroxide to yield 7:3':4'-trimethoxy-3-benzylidene-2:3-dihydro- $\gamma$ -benzopyrone, almost colourless needles, m. p. 139—140°, which is reduced by hydrogen in the presence of platinum black to 7:3':4'-trimethoxybenzylchroman [7:3':4'-trimethoxy-3-benzyl-2:3-dihydro- $\gamma$ -benzopyrone],



colourless, shining needles, m. p. 87°. Similarly, 7-methoxychromanone condenses with piperonal to give the *piperonylidene* derivative, pale yellow, felted needles, m. p. 149°, and with furfuraldehyde to yield the *furfurylidene* compound, needles, m. p. 119—120°.

**7:8-Dimethoxychromanone** [7:8-dimethoxy-2:3-dihydro- $\gamma$ -benzopyrone], colourless leaflets, m. p. 100—101°, is obtained by the reduction of the corresponding chromone with hydrogen in the presence of platinum black; it yields a *semicarbazone*, colourless needles, m. p. 218° (decomp.), an *oxime*, long, shining needles, m. p. 152°, a *piperonylidene* derivative, small, pale yellow needles, m. p. 181°, and a *furfurylidene* compound, pale yellow needles, m. p. 133°. Attempts to condense the chromanone with vanillin methyl ether met with difficulty, but a *substance*, slender, yellow needles, m. p. 133—134°, which is probably 7:8:3':4'-tetramethoxy-3-benzylidene-2:3-dihydro- $\gamma$ -benzopyrone, was isolated in amount too small for identification.

Gallacetophenone dimethyl ether condenses with piperonal in the presence of alcohol and warm 50% aqueous sodium hydroxide solution yielding *piperonylidenegallacetophenone dimethyl ether*,  $\text{OH} \cdot \text{C}_6\text{H}_2(\text{OMe})_2 \cdot \text{CO} \cdot \text{CH} \cdot \text{CH} \cdot \text{C}_6\text{H}_5 \cdot \text{O}_2 \cdot \text{CH}_2$ , deep yellow needles, m. p. 178° (*perchlorate*, dark violet crystals; *acetyl* derivative, yellow leaflets, m. p. 127°), and with furfuraldehyde to give *furfurylidenegallacetophenone dimethyl ether*, golden-yellow needles or leaflets, m. p. 105° (*acetyl* derivative, m. p. 92°). H. W.

**Tannins. IV. Hamameli-tannin. II.** KARL FREUDENBERG and DANIEL PETERS (*Ber.*, 1920, 53, [B], 953—961).—Further investigation has confirmed the previous conclusion (A., 1919, i, 215) that hamameli-tannin is an ester-like compound of gallic acid (2 molecules) and a sugar related to the hexoses. The identification of the latter has not yet been accomplished, but it appears to consist of an almost pure aldo-hexose. It does not give the reactions of a pentose. On the other hand, it differs from the usual hexoses in that it cannot be converted into lævulic acid, but its action towards magenta-sulphurous acid and Fehling's solution indicates that it is a true sugar.

Considerable improvements have been effected in experimental

technique. The hydrolysis is effected by tannase (the preparation of which is described in detail), and the process only goes to completion with solutions containing less than 2.5% of the tannin. The course of the action can be followed for the greater part by polarimetric observations or, preferably, by measurement of the gradual increase of the acidity of the solution. The use of lead carbonate and basic lead acetate for the removal of residual gallic acid has been found to be disadvantageous, since the susceptible hamameli-sugar is thereby extensively changed, and these reagents are now replaced by the washed clay of H. Wislicenus, which is found to adsorb gallic acid and tannin from the cold solution without affecting the sugar. An improved method of purifying hamameli-tannin is fully described. H. W.

**Physical Properties of some Alkaloids.** H. ZEEHUISEN (*Arch. Exp. Path. Pharm.*, 1920, **86**, 342—372).—Some physical properties, such as odour, solubility, surface tension, electrical charge, according to Zwaardemaker's method, etc., of forty-two alkaloids were studied. The results are tabulated together with some of the properties of these alkaloids previously established. S. S. Z.

**Complex Metallic Ammines. III. Dichlorotetrapyridine-cobalt Salts.** THOMAS SLATER PRICE (T., 1920, **117**, 860—865).

**Quinoline-2-, -3-, and -4-sulphonic Acids.** E. BESTHORN and BERTHA GEISSELBRECHT (*Ber.*, 1920, **53**, [B], 1017—1033).—An investigation has been made of the quinoline-2-, -3-, and -4-sulphonic acids which is of particular interest, since quinolines sulphonated in the pyridine nucleus do not appear to have been described previously. In general, the sulphonic acids are well-crystallised substances, the melting points of which are above 270° and have not been determined. They are fairly strong, monobasic acids. The alkali salts are freely soluble in water, as are also the alkaline-earth compounds, although certain of the latter could be obtained in the crystalline condition. The 2-acids are so unstable that they lose sulphur dioxide when their aqueous solutions are boiled, and neither from them nor from the 4-acids was it found possible to prepare the corresponding sulphonyl chlorides or sulphonamides, on account of the readiness with which sulphur dioxide is eliminated. The 3-acids, on the other hand, exhibit a much more normal behaviour.

*Quinoline-2-sulphonic acid*, slender, colourless needles, is prepared by the oxidation of 2-thiolquinoline with nitric acid (D 1.4) or by the action of boiling aqueous sodium sulphite solution on 2-chloroquinoline. The *silver* salt is described. Similarly, 4-chloroquinoline and sodium sulphite yielded *quinoline-4-sulphonic acid*, colourless needles, the *calcium* salt (+4H<sub>2</sub>O) and *silver* salt of which were analysed. *4-Methylquinoline-2-sulphonic acid*, obtained by the oxidation of 2-thiol-4-methylquinoline or from sodium sulphite and 2-chloro-4-methylquinoline, forms slender,

colourless needles, which give 2-hydroxy-4-methylquinoline when boiled with water; the *sodium* and *calcium* salts are described. 2-Methylquinoline-4-sulphonic acid is prepared from 4-thiol-2-methylquinoline or 4-chloro-2-methylquinoline; the *potassium*, *sodium*, *ammonium*, *calcium*, and *silver* salts were investigated.

For the preparation of the 3-sulphonic acids other methods were necessary, since 3-thiolquinoline is unknown, and attempts to prepare 3-thiol-2-methylquinoline from 3-hydroxy-2-methylquinoline were unsuccessful; in addition, the stability of the halogen atom in 3-chloro-2-methylquinoline is such as to render reaction of the substance with sodium sulphite impracticable. The authors have therefore used a method of the Höchst Farbwerke, according to which *o*-aminobenzaldehyde is condensed with sodium acetone-sulphonate in aqueous alkaline solution, and have thus obtained 2-methylquinoline-3-sulphonic acid (the *barium* and *silver* salts, the *sulphonyl chloride*, pale yellow needles, m. p. 121°, and the *sulphonamide*, m. p. 227°, are described). Potassium 2-methylquinoline-3-sulphonate is converted by benzaldehyde and zinc chloride at 180° into 2-styrylquinoline-3-sulphonic acid, which is remarkably stable to acid oxidising agents, but is readily oxidised by potassium permanganate in alkaline solution to a mixture of 2-carboxyquinoline-3-sulphonic acid and 2-aldehydoquinoline-3-sulphonic acid,  $C_{10}H_7O_4NS.H_2O$  (the *oxime*, colourless needles, and *phenylhydrazone* [?] are described); the aldehyde remains unchanged when boiled with fuming nitric acid or with dilute sulphuric acid and chromic acid, but, on the other hand, a boiling aqueous solution of the *calcium* salt is readily oxidised by silver oxide to the *calcium* salt of 2-carboxyquinoline-3-sulphonic acid,  $C_{10}H_5O_5NSCa.4H_2O$  (the *calcium hydrogen* salt is also described). The ready solubility of the free acid in water, combined with the paucity of material, prevented the acid itself from being isolated. The crude acid, however, is converted by concentrated hydrochloric acid at 170° into quinoline-3-sulphonic acid, long, colourless, slender needles ( $+nH_2O$ ); the *barium* salt forms colourless, hydrated needles.

H. W.

**Allyl 2-Phenylquinoline-4-carboxylate.** A. GAMS (U.S. Pat. 1336952).—*Allyl 2-phenylquinoline-4-carboxylate*, long needles, m. p. 30°, b. p. 260°/15 mm., forms a *hydrochloride*, small, citron-yellow needles, m. p. 145–147°, which is instantly hydrolysed by water. The ester is tasteless, and the hydrochloride has a slight sweet taste. The ester can be made by the usual methods, and has therapeutic properties similar to those of the alkyl esters of 2-phenylquinoline-4-carboxylic acid. CHEMICAL ABSTRACTS.

**Influence of Substitution in the Components on the Equilibria in Binary Solutions. XXV. The Binary Systems of Carbazole and Phenols.** ROBERT KREMANN and FERDINAND SLOVAK (*Monatsh.*, 1920, **41**, 23–42. Compare following abstract).—Freezing-point curves have been constructed for the

systems carbazole with  $\alpha$ -naphthol,  $\beta$ -naphthol, catechol, resorcinol, quinol, pyrogallol, the three nitrophenols, 2:4-dinitrophenol, and picric acid respectively. It is shown that the two naphthols, pyrogallol, and the three dihydroxybenzenes do not form compounds with carbazole; in all these cases simple eutectics are formed, as follows:  $\alpha$ -naphthol,  $90.0^{\circ}$  with 7% of carbazole;  $\beta$ -naphthol,  $115.0^{\circ}$  with 9.0% of carbazole; catechol,  $102.0^{\circ}$  with 4.0% of carbazole; resorcinol,  $107.0^{\circ}$  with 7.0% of carbazole; quinol,  $163.0^{\circ}$  with 15% of carbazole; pyrogallol,  $126.0^{\circ}$  with 1% of carbazole. Similar relationships are found for the nitrophenols and 2:4-dinitrophenol, simple eutectics only being formed, as follows: *o*-nitrophenol,  $43.5^{\circ}$  with 3.0% of carbazole; *m*-nitrophenol,  $92.0^{\circ}$  with 5.0% of carbazole; *p*-nitrophenol,  $106.7^{\circ}$  with 6.0% of carbazole; and 2:4-dinitrophenol,  $98.6^{\circ}$  with 17.0% of carbazole. Picric acid forms an equimolecular compound with carbazole, m. p.  $183^{\circ}$ , and this compound forms an eutectic with carbazole at  $181.5^{\circ}$  containing 51% of carbazole, and with picric acid at  $113^{\circ}$  containing 5% of carbazole.

J. F. S.

**Influence of Substitution in the Components on the Equilibria in Binary Solutions. XXIV. The Binary System Acridine with Phenols.** ROBERT KREMANN and FERDINAND SLOVAK (*Monatsh.*, 1920, **41**, 5—21. Compare this vol., i, 570, and preceding abstract).—Freezing-point curves have been constructed for the binary systems of acridine with phenol,  $\alpha$ -naphthol,  $\beta$ -naphthol, quinol, catechol, and resorcinol respectively. It is shown that, in the case of phenol and acridine, two compounds are formed, namely, between two molecules of phenol and one molecule of acridine, m. p.  $87^{\circ}$ , and between two molecules of phenol and three molecules of acridine, m. p.  $101^{\circ}$ . In the case of  $\beta$ -naphthol, two compounds are also formed, between three molecules of  $\beta$ -naphthol and two molecules of acridine, m. p.  $135^{\circ}$ , and between one molecule of  $\beta$ -naphthol and two molecules of acridine, m. p.  $96^{\circ}$ . Acridine and  $\alpha$ -naphthol also form two compounds, an equimolecular compound, m. p.  $115.5^{\circ}$ , and a compound between one molecule of  $\alpha$ -naphthol and two molecules of acridine, m. p.  $97^{\circ}$ . Quinol and resorcinol each form a single compound with acridine of the composition, two molecules of acridine with one molecule of the phenol; these compounds have melting points  $209.5^{\circ}$  and  $179.5^{\circ}$  respectively. In the case of catechol, a single compound is also formed, but this is an equimolecular compound, m. p.  $144.5^{\circ}$ . The affinity of phenol,  $\beta$ -naphthol, and  $\alpha$ -naphthol for acridine increases in the order named.

J. F. S.

**Preparation of *p*-Nitrophenylcarbamide Chloride.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 319969, additional to D.R.-P. 241822; from *Chem. Zentr.*, 1920, ii, 777).—*p*-Nitroaniline is added to a solution of carbonyl chloride in an indifferent solvent, and, if necessary, is further treated with the chloride until the amine hydrochloride has completely disappeared;

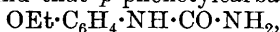


temperatures may be employed which are considerably above that at which dry *p*-nitrophenylcarbamide chloride is transformed into the corresponding carbimide. It is preferable first to dissolve the carbonyl chloride, in part or completely, in the solvent, such as nitrobenzene, benzene, or carbon tetrachloride, and then to add the amine.

H. W.

**Alteration in Taste of the Sweetening Agent, Dulcin [*p*-Phenethylcarbamide] as a Result of Chemical Change.**

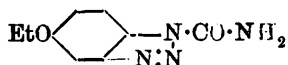
H. THOMS and K. NETTESHEIM (*Ber. deut. pharm. Ges.*, 1920, **30**, 227—250).—It is found that *p*-phenethylcarbamide,



loses its sweetening power when a considerable variety of acidic or basic substituents is introduced into the benzene nucleus.

The only *p*-phenethylcarbamide substituted in the nucleus which has been described previously is that obtained by Berlinerblau by the action of nitrous fumes on an alcoholic solution of dulcin; this compound is now shown to be 3-nitro-*p*-phenethylcarbamide, since it is identical with the product obtained by the successive action of carbonyl chloride and ammonia on 3-nitro-*p*-phenetidine. (3-Nitrophenetidine hydrochloride is obtained as by-product of this action. It commences to dissociate at 130°, and action is complete at 150°. It is extremely readily hydrolysed by water, and the change in colour from the yellow salt to the cinnabar-red base may be conveniently employed in testing for traces of moisture.) 3-Nitro-*p*-phenethylcarbamide may also be obtained by the action of dilute nitric acid on dulcin at the ordinary temperature. (The readiness with which dulcin is converted into its intensely yellow nitro-derivative forms the basis of a convenient and rapid method of distinguishing between dulcin and other sweetening agents.) 2-Nitro-*p*-phenetidine is similarly transformed by carbonyl chloride and ammonia into 2-nitro-*p*-phenethylcarbamide, long, yellow, shining needles, m. p. 178·5° after softening at 176°. This substance is also obtained by the action of a cold mixture of nitric acid (53%) and concentrated sulphuric acid on dulcin, but the yield is only 60%, as a considerable amount of the latter is destroyed. It cannot be conveniently prepared from 2-nitro-*p*-phenetidine hydrochloride and potassium cyanate in boiling aqueous solution, since the main product of this action is dinitro-*p*-diphenethylcarbamide,  $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_3[\text{NO}_2]\cdot\text{OEt})_2$ , yellow needles, m. p. 201°. 3-Nitroso-*p*-phenethylcarbamide is conveniently prepared by the addition of the requisite quantity of sodium nitrite solution to a suspension of finely powdered dulcin in much concentrated hydrochloric acid; it forms pale yellow needles, which decompose at 51—52°. 3-Amino-*p*-phenethylcarbamide, needles, decomposing at 179°, is prepared by the reduction of the corresponding nitro-compound with tin and hydrochloric acid; the hydrochloride, colourless leaflets, decomposing slowly at 170°, the sulphate, prisms, and the acetyl derivative, coarse, colourless needles, m. p. 181°, are described. When the salts are treated with nitrous acid, the

diazonium compound is produced, which rapidly passes into the azimino-derivative (annexed formula), slender needles, m. p. about 141° (decomp.) after softening at 138°.



Similarly, 2-nitro-*p*-phenethylcarbamide is reduced by tin and hydrochloric acid to 2-amino-*p*-phenethylcarbamide, colourless needles, m. p. 202° (the hydrochloride [ $+ \text{H}_2\text{O}$ ] and acetyl derivative, slender, silky needles, m. p. 217—218°, are described). Nitrous acid converts the substance into a dark brown dye. *p*-Phenethylcarbamide-2-sulphonic acid is prepared by the action of fuming sulphuric acid on dulcin at 50—60°; the sparingly soluble lead and the sodium salt were analysed. The constitution of the compound is proved by its formation from a boiling aqueous solution of carbamide nitrate and *p*-phenetidine-2-sulphonic acid. It could not be transformed into the corresponding phenol by fusion with potassium hydroxide. 2-Chloro-*p*-phenethylcarbamide, small, matted needles, m. p. 148°, is obtained in almost quantitative yield from 2-chloro-*p*-phenetidine hydrochloride and potassium cyanate. The similarly prepared 2-bromo-*p*-phenethylcarbamide forms long prisms, m. p. 156°. A dichloro-*p*-phenethylcarbamide, needles, m. p. 200°, is obtained from dichloro-*p*-phenetidine by the successive action of carbonyl chloride and ammonia.

H. W.

**The Sweetening Power of Derivatives of *p*-Hydroxyphenylcarbamide.** F. BOEDECKER and R. ROSENBUSCH (*Ber. deut. pharm. Ges.*, 1920, **30**, 251—258).—The authors have attempted to obtain a sweetening agent analogous to dulcin (*p*-phenethylcarbamide), but possessing greater sweetening power and greater solubility in water, and have therefore prepared hydroxy-*p*-ethoxyphenylcarbamide,  $\text{HO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , and  $\beta\gamma$ -dihydroxy-*p*-propoxyphenylcarbamide,  $\text{HO} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ . An improvement in the solubility in water is noticed in either case, but the former compound is less sweet than dulcin and has a bitter after-taste, whilst the latter is not sweet.

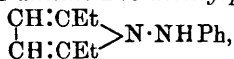
Hydroxy-*p*-ethoxyphenylcarbamide, plates, m. p. 160°, is obtained by the action of ethylene chlorohydrin on *p*-hydroxyphenylcarbamide in the presence of sodium ethoxide or, alternatively, by condensing ethylenechlorohydrin with *p*-nitrophenol to *p*-nitrophenyl hydroxyethyl ether, pale yellow needles, m. p. 94—95°, and reducing the latter with zinc dust and hydrochloric acid to *p*-aminophenyl hydroxyethyl ether hydrochloride, needles, m. p. 204—205°, and converting the amino-ether into the corresponding carbamide by an aqueous solution of calcium cyanate.  $\beta\gamma$ -Dihydroxy-*p*-propoxyphenylcarbamide, needles, m. p. 156—157°, is prepared from *p*-hydroxyphenylcarbamide and  $\alpha$ -monochlorohydrin.

*p*-Hydroxyphenylcarbamide reacts with chloroacetamide at 100—110° in the presence of sodium methoxide, yielding *p*-carbamidophenoxyacetamide,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$ , small leaflets, m. p. 264° after previous softening; it is tasteless.

H. W.

**The Iodoamidines.** J. BOUGAULT and P. ROBIN (*Compt. rend.*, 1920, 171, 38—40).—Benzamidine reacts with iodine in the presence of dilute aqueous sodium hydroxide to give *iodobenzamidine*, m. p. 117°, which is apparently a derivative of hypoioidous acid. It reacts with potassium iodide in the presence of hydrochloric acid, the whole of its iodine being liberated, thus showing that the iodine is linked directly with the nitrogen and is not a substituent of the benzene ring. Anisamidine and piperonamidine give similar crystalline iodoamidines. W. G.

**Action of Substituted Hydrazines on the Acyclic  $\alpha\delta$ -Diketones.** E. E. BLAISE (*Compt. rend.*, 1920, 171, 34—36).—Whilst hydrazine gives with acyclic  $\alpha\delta$ -diketones a mixture of derivatives of pyridazine and tetrahydropyridazine, the substituted hydrazines give pyrrole derivatives. Thus *s*-dipropionylethane gives with phenylhydrazine 1-anilino-2:5-diethylpyrrole,



m. p. 65·5°. Similarly, with phenylmethylhydrazine, it yields 1-methylanilino-2:5-diethylpyrrole, b. p. 162°/16 mm., which, when reduced with zinc and hydrochloric acid in acetic acid solution, gives aniline and 2:5-diethylpyrroline, b. p. 154°/760 mm. or 62°/28 mm., giving a *platinichloride*, m. p. 180° (decomp.); an *aurichloride*, m. p. 100—101°, and a *picrate*, m. p. 97—98°. Dipropionylethane reacts with ammonia to give 2:5-diethylpyrrole, b. p. 100°/29 mm., giving an *oxime*, m. p. 155°. On reduction, the pyrrole gives the 2:5-diethylpyrroline described above. W. G.

**Coloured Sensitisers Derived from Quinolines, Quinaldines, and Lepidines containing Dimethylamino- and Diethylamino-groups.** H. BARBIER (*Bull. Soc. chim.*, 1920, [iv], 27, 427—439).—6-Dimethylaminoquinoline gives an *ethiodide*, m. p. 212°, and an impure *isomeride*, m. p. 170°, in which the ethyl iodide is probably attached to the nitrogen of the  $\cdot\text{NMe}_2$  group.

When *p*-phenylenediethyldiamine, glycerol, sulphuric acid, and nitrobenzene are boiled together for three hours, 6-diethylaminoquinoline, b. p. 192—193°/20 mm., is obtained, giving a *hydrochloride*, a *platinichloride*, m. p. 280°, a *picrate*, m. p. 196°, a *methiodide*, m. p. 148°, and an *ethiodide*, m. p. 159°.

By the action of paraldehyde on *p*-phenylenedimethyldiamine in hydrochloric acid solution, 6-dimethylamino-2-methylquinoline, m. p. 101°, b. p. 319°/760 mm., is obtained, yielding a *hydrochloride*, a *sulphate*, a *platinichloride*, m. p. 199° (decomp.), a *mercurichloride*, m. p. 202°, two isomeric *methiodides*, m. p. 230° and 190° respectively, and two *ethiodides*, m. p. 226° and 100° respectively, of which the less fusible compound has the alkyl iodide attached to the ring nitrogen, whilst in the more fusible compound it is united to the alkylamino-nitrogen. Dimethylaminomethylquinoline also gives a *di-ethiodide*.

By the action of a mixture of acetone and formaldehyde saturated with hydrogen chloride on *p*-phenylenedimethyldiamine in hydrochloric acid, 6-dimethylamino-4-methylquinoline, m. p. 71°,

b. p. 330°, is obtained, giving a *hydrochloride*, a *platinichloride*, m. p. 200°, a *mercurichloride*, m. p. 206°, a *methiodide*, and probably two *ethiodides*.

The alkyl iodides of quinoline, and of 2- and 4-methylquinolines containing a dialkylamino-group, give a series of new colouring matters when condensed either among themselves or with alkyl iodides of other bases. Thus, 6-dimethylaminoquinoline ethiodide yields a cyanine when condensed with 2:6-dimethylquinoline ethiodide. In a similar way, the author has prepared cyanines by condensing the following mixtures: (b) 6-Dimethylaminoquinoline ethiodide and 6-dimethylamino-2-methylquinoline ethiodide. (c) 6-Diethylaminoquinoline ethiodide and 2:6-dimethylquinoline ethiodide. (d) 2:6-Dimethylquinoline ethiodide and 6-dimethylamino-2-methylquinoline ethiodide. (e) 6-Dimethylaminoquinoline methiodide and 2:6-dimethylquinoline methiodide. (f) 2:6-Dimethylquinoline methiodide and 6-dimethylaminoquinoline amyliodide. (g) 6-Dimethylaminoquinoline ethiodide and 2:6-dimethylquinoline methiodide. (h) 6-Dimethylaminoquinoline methiodide and 2:6-dimethylquinoline ethiodide. (i) 6-Dimethylaminoquinoline methiodide and 6-dimethylamino-2-methylquinoline methiodide. (j) 6-Dimethylaminoquinoline ethiodide and 4-methylquinoline ethiodide. (k) 6-Dimethylaminoquinoline ethiodide and 6-dimethylamino-4-methylquinoline ethiodide. (l) 6-Dimethylamino-2-methylquinoline methiodide by itself. (m) 6-Dimethylamino-2-methylquinoline ethiodide by itself. (n) 6-Dimethylamino-4-methylquinoline by itself. (o) Dimethylaminoquinoline ethiodide, 2:6-dimethylquinoline ethiodide and formaldehyde. (p) Dimethylaminoquinoline ethiodide, dimethylamino-2-methylquinoline ethiodide and formaldehyde. (q) Dimethylamino-2-methylquinoline ethiodide by itself in the presence of formaldehyde. (r) *p*-Dimethylaminobenzaldehyde in turn with dimethylamino-2-methylquinoline methiodide and ethiodide, and dimethylamino-4-methylquinoline methiodide and ethiodide.

All these cyanines containing the active auxochrome group,  $\text{NMe}_2$  or  $\text{NEt}_2$ , are of interest in photography as sensitisers.

W. G.

**Condensation of 1-Phenyl-3-methyl-5-pyrazolone with Aldehydes and Ketones.** S. C. CHATTERJEE and B. N. GHOSH (*Proc. Asiatic Soc. Bengal*, 1919, 15, cxxxii—cxxxiii).—When 1-phenyl-3-methyl-5-pyrazolone is heated with aldehydes in molecular proportions, condensation usually takes place with the elimination of water. The compounds thus obtained have the general

formula  $\text{CHR}:\text{C} \begin{smallmatrix} \text{CO}-\text{N}^{\text{Ph}} \\ \text{CMe}:\text{N} \end{smallmatrix}$ . These substances contain the chromophore  $\cdot\text{CO}:\text{C}:\text{C}$ , and are highly coloured. The present paper describes how aldehydes may be made to unite with pyrazolone, without the elimination of water, to form the intermediate additive hydroxyl compounds,  $\text{OH}\cdot\text{CHR}\cdot\text{CH} \begin{smallmatrix} \text{CO}-\text{N}^{\text{Ph}} \\ \text{CMe}:\text{N} \end{smallmatrix}$ . The chromo-

phoric group,  $\cdot\text{CO}\cdot\text{C}\cdot\text{C}$ , is absent in them, and necessarily they are either colourless, or at any rate much less coloured than the corresponding unsaturated compounds. An attempt to synthesise pyranol derivatives from the pyrazolone and *o*-hydroxy-aldehydes is also described. Some new condensation products with aldehydes and ketones have been prepared, and in this connexion it has been pointed out that the aliphatic ketones are much less reactive than those of the aromatic series.

CHEMICAL ABSTRACTS.

**Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XXIII. The Binary System Antipyrine-Benzoic Acid.** ROBERT KREMANN and HERMANN MARKTL (*Monatsh.*, 1920, **41**, 1—4. Compare A., 1919, ii, 458).—Freezing-point curves of the binary mixture benzoic acid and antipyrine have been made, from which it is seen that these two substances form a single equimolecular compound, m. p.  $66^{\circ}$ ; this compound forms an eutectic with benzoic acid at  $59\cdot5^{\circ}$  containing 50·5% of antipyrine, and one with antipyrine containing 63·5% antipyrine at  $59\cdot5^{\circ}$ . These results show that compounds such as salipyrine are due to combination of the carboxyl group with the antipyrine, and not to the phenolic group, for although phenol does form an equimolecular compound with antipyrine, it is a much weaker compound than that formed in the present experiments.

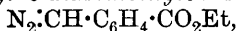
J. F. S.

**Condensation of Benzoin with Diamines.** S. C. CHATTERJEE and B. N. GHOSH (*Proc. Asiatic Soc. Bengal*, 1919, **15**, cxxxi—cxxxii).—With the object of preparing substituted naphthadipyridines or pyridinonaphthapyrroles, the reaction between benzoin and some of the naphthylenediamines has been studied, using the corresponding amine hydrochlorides as condensing agents. The reaction took place in the manner desired only in the case of 1:4- and 1:5-diamines, a mol. of the diamine combining with 2 mols. of benzoin with the elimination of 4 mols. of water. There are three possible formulæ for each of these substances, and, although no conclusive proof is available, on the strength of indirect evidence it has been suggested that each of the two nitrogen atoms in both these substances forms part of a six-membered ring. Contrary to expectation, the 1:2-diamine yielded a product which appears to be identical with Fischer's diphenyldihydronaphthaquinoxaline (A., 1893, i, 284). Incidentally, the reaction between benzoin and benzidine was also studied, but in this case the closing of the ring did not take place, the compound obtained having the structure  $\text{C}_{12}\text{H}_8(\text{NH}\cdot\text{CHPh}\cdot\text{COPh})_2$ . An attempt was made to close the ring by boiling with acetic anhydride, but this only resulted in the formation of a diacetyl derivative.

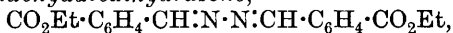
CHEMICAL ABSTRACTS.

**The Constitution of Yellow Sulphide Dyes.** JATINDRA KUMAR MAZUMDER and EDWIN ROY WATSON (T., 1920, **117**, 830—834).

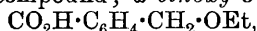
**Decomposition of Nitroso-compounds. II.** WILLIAM A. NOYES and JAMES A. COSS (*J. Amer. Chem. Soc.*, 1920, **42**, 1280—1286. Compare Oppé, A., 1913, i, 534).—When an ice-cold alcoholic solution of nitrosophthalimidine is treated with alcoholic sodium hydroxide, *ethyl o-diazomethylbenzoate*,



red crystals, m. p.  $39^\circ$ , separate, but at the ordinary temperature after two to three days, or on warming, nitrogen is evolved, and *ethyl phthalaldehydatedihydrazone*,



yellow crystals, m. p.  $145^\circ$ , is produced; this compound is decomposed by hydrochloric acid at  $130^\circ$  into phthalazone and phthalaldehydic acid. *Ethyl o-ethoxy-o-toluate*,  $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OEt}$ , an oil,  $D_{25}^{25}$  1.059,  $n_D^{25}$  1.49556, is produced by boiling an alcoholic solution of the diazo-compound; *o-ethoxy-o-toluic acid*,



melts at  $84.5^\circ$ . Similarly, the product of the action of sodium hydroxide on nitrosoaminolauronic anhydride (Noyes and Taveau, A., 1904, i, 807) is the dihydrazone of camphononic acid, which gives camphononic acid on hydrolysis, accompanied by *ethoxy-lauronic acid*,  $\text{OEt}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}_2\text{Et}$ , b. p.  $113\text{—}115^\circ/3$  mm. J. K.

**The Behaviour of Albumins and Antitoxins towards the Electric Current and the Isolation of Pure Antitoxic Albumin from Diphtheria Serum by the Electro-osmotic Method.** W. G. RUPPEL (*Ber. deut. pharm. Ges.*, 1920, **30**, 314—328).—If the blood serum of a normal animal is subjected to the action of an electric current in a cell which is divided into three partitions by suitable semipermeable membranes, and is so arranged that the middle cell contains the serum whilst the outer ones contain pure water in which the electrodes are placed, the fission of the electrolytes and wandering of the ions is first observed, whilst also a number of organic substances, such as amino-acids and degradation products of the albumins, are removed. As soon as the isoelectric point has been reached, the separation of euglobulin commences in the middle cell, and the reaction of the serum passes from neutral or faintly alkaline to acid. After removal of euglobulin, the separation of paraglobulin and albumins can be electrically effected, since the latter are more highly electrically charged, and therefore have a higher velocity of migration. The process can also be applied to the preparation of a pure antitoxic albumin, since it is found that the antitoxins are not in any way damaged or weakened by the electric current. In diphtheria serum, the antitoxin is mainly combined with the paraglobulin, whilst the euglobulin contains only small amounts of antitoxin, and the albumin practically none. The procedure has the advantage over precipitation methods that the usual inactive ingredients of the serum of immunised animals are also removed, whilst the danger of bacterial impurities can easily be avoided.

H. W.

**Tyrosine and the Dibasic Amino-acids in the Proteins of Yeast.** PIERRE THOMAS and ANDRÉ CHABAS (*Compt. rend.*, 1920, **170**, 1622—1625).—An examination of the two proteins, cerevisin and zymocasein, previously found in yeast (compare A., 1913, i, 942, 1026), shows that cerevisin contains 4.13% of tyrosine, 6.26% of glutamic acid, and about 1% of aspartic acid. Zymocasein contains 2.85% of tyrosine, 0.94% of glutamic acid, and about 1% of aspartic acid. In the estimation of glutamic acid, the authors recommend the recrystallisation of its hydrochloride from 96% alcohol, in order to free it from ammonium chloride.

W. G.

**Hæmoglobins.** J. THONNARD (*Compt. rend. Soc. Biol.*, 1920, **83**, 441—442; from *Chem. Zentr.*, 1920, i, 895).—In the reduction of oxyhæmoglobin with ammonium sulphide for distinguishing it from carbon monoxide hæmoglobin, the concentration of the reducing agent, the temperature, and the origin of the blood are of considerable importance. Experiments with human and animal blood are described. Under similar conditions, the oxyhæmoglobins of warm-blooded animals are much more stable than those of cold-blooded animals.

H. W.

**Carbon Monoxide Hæmoglobin.** J. THONNARD (*Compt. rend. Soc. Biol.*, 1920, **83**, 443—444; from *Chem. Zentr.*, 1920, i, 895).—The times have been measured which, at different temperatures and with a uniform current of gas, are necessary for the conversion of carbon monoxide hæmoglobin by hydrogen into reduced hæmoglobin and by oxygen into oxyhæmoglobin, the experiments being performed with the blood of man, ox, and carp. The results show a complete parallelism between these actions and the stability of oxyhæmoglobin towards ammonium hydrogen sulphide (preceding abstract).

H. W.

**The Production and Properties of Pathological Melanin.** E. SALKOWSKI (*Arch. path. Anat.*, 1920, **227**, 121—137).—Melanin was obtained from the intestinal tract and from tumours. A total of 995 grams of intestine yielded only 0.4406 gram of melanin, or 0.044%. In the preparation of melanin it is necessary to avoid heating with concentrated hydrochloric acid, since this may lead to the formation of melanoidin. The last traces of protein and fat can be removed by heating with glacial acetic acid. By this method, melanin is obtained in two fractions, one soluble in dilute sodium hydroxide, another insoluble even in 15% sodium hydroxide. By keeping, the soluble portion also tends to become insoluble. Melanin contains sulphur, which is firmly bound. It is resistant to oxidising agents, but is completely destroyed by permanganate in alkaline solution and by a mixture of potassium dichromate and sulphuric acid. Melanin consists in large measure of atom complexes belonging to the cyclic and heterocyclic series, but also contains aliphatic molecules.

CHEMICAL ABSTRACTS.

**Melanin and the Brown Endogenous Pigments.** B. BRAHN and MARTHA SCHMIDTMANN (*Arch. path. Anat.*, 1920, **227**, 137—152).—I. *Melanin*.—Melanin obtained from human tumours showed the following elementary analysis: C 51·92, H 5·21, N 11·03, S 3·42%. Melanoidin from horn contained: C 52·85, H 5·91, N 10·04, S 5·41%. Melanin is believed to be 3:4-dihydroxyphenylcysteine,  $\text{C}_6\text{H}_3(\text{HO})_2\cdot\text{CH}_2\cdot\text{C}(\text{SH})(\text{NH}_2)\cdot\text{CO}_2\text{H}$ . II. *Endogenous pigment*.—The endogenous brown pigments are insoluble in ethyl alcohol and ether. The ability of these pigments to be stained with fat stains is due to extraneous material, and not to fatty acids contained within them. The pigment obtained from a heart showing brown atrophy was physically and chemically identical with melanin. III. *Relation of melanin to adrenaline*.—Melanin, like adrenaline, causes vasoconstriction. It does not cause hyperglycemia when injected intravenously. The action of adrenaline on the heart differs from that of melanin.

## CHEMICAL ABSTRACTS.

**Esterification of  $\alpha$ -Amino-acids.** H. A. SHONLE and H. H. MITCHELL (*J. Amer. Chem. Soc.*, 1920, **42**, 1265—1277).—The progress of esterification by the process of Osborne and Jones (A., 1910, i, 447) of individual amino-acids, and of mixtures obtained by the acid hydrolysis of casein, vignin, gelatin, and vegetable albumin, has been studied. The method depends on a determination of both the mineral and the unesterified amino-acids by the method of Sørensen (A., 1908, i, 115), and of the mineral acid alone by a Volhard estimation of chloride ion, allowance being also made for acidity due to addition of silver nitrate, when this has been used for purposes of decolorisation. This was, however, best accomplished by means of barium hydroxide and aluminium sulphate, which are preferable to sodium carbonate and potassium alum (Denis, A., 1911, ii, 163), because they can be quantitatively removed. Alanine can be esterified to the extent of 96%, lysine 82%, glutamic acid 85%, and a mixture of amino-acids 90%. Determination of the total amino-acids after prolonged acid hydrolysis shows that a considerable proportion, 36% of those from casein, undergoes esterification during the removal of water from the crude acids preparatory to esterification by repeated evaporation with alcohol. Of the subsequent esterification, most occurred during the first hour, after which it progressed slowly until equilibrium was reached. There is no unesterifiable residue.

J. K.

**Mechanism of Enzyme Reaction.** EIICHI YAMASAKI (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, **9**, 137—142).—A theoretical paper in which a number of hypotheses put forward to explain the mechanism of enzyme action are discussed.

J. F. S.

**The Influence of Hydrogen-ion Concentration on the Inactivation of Pepsin Solutions.** JOHN H. NORTHROP (*J. gen. Physiol.*, 1920, **2**, 465—470).—Pepsin in solution at 38° is most



stable at a hydrogen-ion concentration of about  $P_H$  5.0, this point being independent of the anion of the acid used and of the purity of the enzyme solution. Increasing the hydrogen-ion concentration above  $P_H$  5.0 causes a slow increase in the rate of destruction of pepsin, whilst decreasing the hydrogen-ion concentration causes a very rapid increase in the rate of destruction of the enzyme.

The existence of an optimum range of hydrogen-ion concentration for the digestion of proteins by pepsin cannot be explained on the grounds of destruction of the enzyme by either too weak or too strong acid.

W. G.

**The Effect of the Concentration of Enzyme on the Rate of Digestion of Proteins by Pepsin.** JOHN H. NORTHPROP (*J. gen. Physiol.*, 1920, 2, 471—498).—In certain cases, it is found that the rate of digestion of proteins by pepsin is not proportional to the total concentration of the pepsin, and it is suggested that this is due to the enzyme being in equilibrium with another substance, which the author, for convenience, calls peptone. This equilibrium is expressed by the law of mass action, according to the equation  $K = \text{concentration pepsin} \times \text{concentration peptone} / \text{concentration pepsin-peptone}$ , it being assumed that only the uncombined pepsin affects the hydrolysis of the protein. This was expressed as a differential equation, and was found to agree with experimental results. Pepsin inactivated by alkali enters the equilibrium to the same extent as active pepsin. Where the concentration of peptone is large with respect to that of the pepsin, that of the substrate being relatively constant, the equation simplifies to Schütz's rule,  $x = K \sqrt{TEA}$ , where  $x$  = amount of substrate digested,  $T$  = time,  $E$  = concentration of pepsin, and  $A$  = concentration of substrate.

An integral equation, identical with that of Arrhenius for the action of ammonia on ethyl acetate, is obtained, which holds for the entire course of the digestion, except for the first few minutes, with varying enzyme concentration.

It is shown that there are many analogies between the action of pepsin on albumin solutions and that of toxins on an organism.

W. G.

**Properties of a Specially Prepared Enzymic Extract, Polyzime, and comparison of its Starch Liquefying Power with that of Malt Diastase.** JOKICHI TAKAMINE, jun., and KOKICHI OSHIMA (*J. Amer. Chem. Soc.*, 1920, 42, 1261—1265).—Polyzime is an aqueous extract of diastatic enzymes, D 1.03—1.06, containing many other enzymes, made by a specially prepared culture of *Aspergillus oryzae* on media, consisting mainly of wheat bran. Its amylolytic power by Wohlgemuth's method is  $D_{30}^{40^\circ}$  3.000;  $D_{24}^{50^\circ}$  115.000; whilst Lintner's saccharogenic value at 21° is 43, and at 50°, 150. Its diastatic power remains unchanged at the ordinary temperature for six months, but is diminished after three hours above 40°. Its chemical composition is also given. J. K.

**Chemical Kinetics of Catalase. II. Catalase from a Germinated Bean: *Glycine hispida maxim*.** EIICHI YAMASAKI (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, **9**, 59—73. Compare this vol., i, 194).—The enzyme from germinated beans, *Glycine hispida maxim*, was obtained as a dry, very active powder by digesting the crushed beans with distilled water saturated with toluene. The rate of decomposition of hydrogen peroxide by means of the catalase, *G. hispida* has been studied at 0°, 10°, 18°, and 25°, and it is found that the reaction follows the theory previously put forward for the catalase *Phyllostachys mitis*, Riv. (this vol., i, 453). There is a remarkable difference between the two kinds of enzyme. The temperature-coefficient of the rate of decomposition is  $\beta_k = 1.40$  for *P. mitis* and 1.85 for *G. hispida*. The difference observed is much too great to be attributed to the effects of the coexisting proteins. To test this point, the reaction was carried out with the enzyme containing different quantities of the coexisting soluble proteins, when no difference was found in the value of  $k'$ . It seems probable that catalase is a common name for a group of enzymes which have the power of catalysing hydrogen peroxide. These enzymes have different stabilities by which they may be recognised, and they probably have different physical properties. J. F. S.

**Chemical Kinetics of Catalase. III. Effect of Chemical Reagents on the Kinetics of Catalase.** EIICHI YAMASAKI (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, **9**, 75—88. Compare preceding abstract).—The effect of adding small quantities of various substances to the reaction mixture of catalase and hydrogen peroxide has been studied at 0°. The experiments were carried out by adding to 18 c.c. of water 2 c.c. of a mixture of the catalase and the other chemical substance; this is kept at 0° for some time, usually about an hour, and then 4 c.c. of 0.1*N*-hydrogen peroxide is added. The rate of reaction is then measured in the usual way. The reactions are controlled by a similar procedure, but leaving out the foreign substance. The influence of the added substance is calculated from the equations,  $r_1 = kE_0/kE_{0(\text{control})}$ ;  $r_2 = k'/k'_{(\text{control})}$  in which  $kE_0$  and  $k'$  are the initial activity and decomposition constants in the presence of the added substance, and  $kE_{0(\text{control})}$  and  $k'_{(\text{control})}$  are the same values in the absence of the control;  $r_1$  and  $r_2$  are the coefficients of depressions of the activity. It is found that mercuric chloride, potassium cyanide, hydroxylamine, and phenylhydrazine entirely stop the reaction; strong oxidising agents such as potassium chlorate, potassium nitrate, and potassium dichromate retard the reaction very much; manganese sulphate increases the reaction, as also do soluble starch, glycine, and sucrose; dextrose is entirely without action. All other substances used retard the reaction; the order of the effect, starting with the greatest retardation, is aniline, silver sulphate, ferric alum, acetonitrile, ammonium molybdate, potassium dichromate, copper sulphate, yellow phosphorus (15 c.c. sat. sol.), chrome alum, potassium nitrate, mercuric cyanide, potassium chlorate, alanine, quinine, sodium

carbonate ( $N/100$ ), brucine, sodium oleate, salicin, potassium chloride, asparagine, arsenious acid, menthol (15 c.c. sat. soln.), cobalt sulphate, urethane, ammonium vanadate, ammonium sulphate ( $N/1875$ ), dextrose. The concentration used was  $N/1200$ , except where the contrary is stated. The effects of the electrolytes are attributed to oxidation, adsorption, or combination with the enzyme, and, as a secondary action, coagulation. J. F. S.

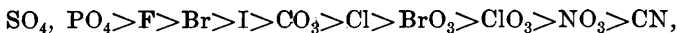
**Chemical Kinetics of Catalase. IV. Catalase from the Blood of Cattle.** EIICHI YAMASAKI (*Sci. Rep. Tôhoku. Imp. Univ.*, 1920, 9, 89—95. Compare preceding abstracts).—The reaction between catalase from the blood of cattle and hydrogen peroxide has been examined at  $0^\circ$ ,  $12.5^\circ$ ,  $10^\circ$ ,  $18^\circ$ , and  $25^\circ$ . The reaction is similar in every respect to that observed with catalase from other sources. The temperature-coefficients are  $k=1.28$  and  $k'=1.63$ , which indicate that the present catalase differs from those previously examined.

Investigations with catalase from various sources show that the decomposition of the enzyme is approximately proportional to that of the hydrogen peroxide. When the enzyme is kept in the solid state for about a year, it is changed into a less active variety. The rate of reaction is expressed by  $-dC/dt = kEC$  and

$$(-dE/dt)/(-dC/dt) = k'/k.$$

The course of the reaction may be attributed to the fact that most of the labile kind of catalase had decomposed and that the chief rôle was taken by the stable variety. Similar behaviour was also found with solutions of the ferments which had previously been treated with hydrogen peroxide. This may also be attributed to the fact that the labile form decomposes more rapidly with hydrogen peroxide than the stable form. J. F. S.

**Action of Poisons on an Enzymatic Process. VI. Comparative Experiments on the Action of Certain Potassium and Sodium Compounds.** C. G. SANTESSON (*Skand. Arch. Physiol.*, 1920, 39, 236—256; from *Chem. Zentr.*, 1920, iii, 18—19).—The influence of a series of potassium and sodium salts on the ability of the catalase of frog's muscle to decompose hydrogen peroxide has been studied. In general, action of a salt depends on the anion rather than the cation. The anions may be approximately arranged in the following order:



in which the first member is least and the last most potent. The following series is established for the cations of a number of chlorides:  $\text{Mg} > \text{Zn} > \text{Ba} > \text{K} > \text{Sr} > \text{Ca} > \text{Na} > \text{Fe}$ . The order is not invariably maintained with different concentrations. H. W.

**Urease.** ARNOLD HAHN (*Ber. deut. pharm. Ges.*, 1920, 30, 329).—In their recent communication, Wester and Pin Yin Yi appear to

have completely overlooked the fact that certain of the results which they describe have been obtained previously by the author.  
H. W.

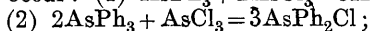
**Chemical Kinetics of Urease.** EIICHI YAMASAKI (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, 9, 97—136).—The decomposition of urea by urease has been investigated under various conditions. The enzyme used was obtained from the soja bean by powdering the beans, extracting the powder with water saturated with toluene, filtering, and precipitating the filtrate with alcohol. The precipitate is washed with absolute alcohol and dried in a vacuum over calcium chloride. It is shown that when the reaction was examined in a faintly acid solution in the presence of a constant stream of carbon dioxide, the reactions  $\text{CO}(\text{NH}_2)_2 \rightarrow \text{NH}_2 \cdot \text{CO}_2\text{NH}_4 \rightarrow (\text{NH}_4)_2\text{CO}_3$  take place with about the same velocity. Since the initial velocity  $[-dc/dt]_{t=0}$  is unaffected by any factor, the velocity constant  $k_1$  of the first reaction is determined by  $[-dC/dt]_{t=0}/C_0 = k_1$ , from which it is shown that  $k_1$  is proportional to the concentration of the urease, when the initial concentration of the urea is taken as constant. But it is a somewhat complicated function of the initial concentration of the urea, even though a constant quantity of urease is used at the start; the relationship is  $1/k_0(k_0 - k) = 8.2C_0^{0.8}$ , where  $k_0$  is the velocity constant for  $C_0 = 0.002$ ;  $k_0$  is taken as the standard because the effect of urea on urease can be reasonably neglected in such a dilute solution. The constant  $k$  of the second reaction seems to be independent of the initial concentration of urea, but it is approximately proportional to that of the urease. Although the ferment forms an heterogeneous system with the substrate, the reaction is homogeneous, that is, the decomposition of the substrate does not take place in the enzyme phase; at the same time, the rate of hydrolysis is not that with which the substrate diffuses into the enzyme phase, because the reaction is not affected by stirring. The mechanism of the reaction does not consist in the decomposition with a measurable velocity of an intermediate compound formed instantaneously by the reacting components, as is generally accepted. Further, the enzyme and the substrate do not form an intermediate compound with a measurable velocity, and the latter is not decomposed into the products of reaction and the enzyme as is assumed by van Slyke and Cullen. It is a simple catalytic action carried on in the substrate phase. The activity of the catalyst, however, is instantaneously diminished in an irreversible manner by the substrate, according to the equation given above. The experimental results are calculated by means of the formulæ  $C_{M_1} = C_0 e^{-k_1 t}$ ;  $C_{M_2} = C_0 \cdot k_1 / (k_2 - k_1) \cdot (e^{-k_1 t} - e^{-k_2 t})$ ;  $C_{M_3} = C_0 [1 - 1/(k_2 - k_1) \cdot (k_2 e^{-k_1 t} - k_1 e^{-k_2 t})]$ , and it is found that there is a fair agreement between the calculated and observed values. The temperature-coefficients for  $k_1$  and  $k_2$  are 1.90 and 1.93 respectively. The addition of electrolytes diminishes the activity of the enzyme, due to the adsorption of them by the enzyme. The effects are calculated by Freundlich's formula for hydrochloric acid,

$h = 1/k_0 \cdot (k_0 - k_1) = 107C^{0.5}$ ; for mercuric chloride,  $h = 108.3C^{0.3}$ ; and for silver sulphate,  $h = 1000C^{0.63}$ . The effect of alkalis is reversible, but that of acids is irreversible. Consequently, the Michaelis relationship,  $\psi'/\psi = 1/(1 + [OH]/q)$ , is applicable to the alkalis, but  $\psi'/\psi = 1/(1 + q/[H'])$  does not hold for acids, because the action of the hydrogen ion is irreversible. J. F. S.

**The Action of Iodine on Arsenious Acid and its Phenyl Derivatives.** PAUL FLEURY (*Bull. Soc. chim.*, 1920, [iv], 27, 490—507).—Iodine reacts with arsenious acid and with the corresponding tervalent phenyl derivatives of arsenic (phenylarsine, diphenylarsine, and triphenylarsine) in the same manner, converting them all into the corresponding arsenic compounds. The action is, however, a balanced one, the hydriodic acid formed tending to reduce the arsenic compounds. In aqueous solution, if their insolubility did not oppose the action, the oxidation of the three phenylarsines would be complete under conditions where arsenious acid would give an equilibrium reaction. Phenylarsine is, however, very sharply distinguished from the di- and tri-phenylarsines, both in the velocity of its oxidation and the equilibrium attained under uniform conditions. The four compounds form a continuous series, in which the oxidisability by iodine increases from arsenious acid up to triphenylarsine. It is of interest to note that both potassium iodide and alcohol, far from diminishing the reducing action of hydriodic acid on the arsenic compounds, rather increase the reduction, and if both iodide and alcohol are present in sufficient concentration, may totally invert the action.

W. G.

**Production of Aromatic Arsenic Compounds [Mono- and Di-aryl Arsenious Haloids].** (SIR) WILLIAM JACKSON POPE (*Brit. Pat.* 142880).—Mono- and di-aryl arsenious haloids are obtained by bringing an arsenious haloid in the liquid or vapour phase into intimate contact with a triarylsarsine heated to a high temperature under ordinary atmospheric pressure. According to the proportion of arsenious haloid employed, reactions expressed by the following equations, in the typical case of the phenyl arsenic chlorides, occur: (1)  $AsPh_3 + 2AsCl_3 = 3AsPhCl_2$ ;



(3)  $AsPh_3 + AsCl_3 = AsPh_2Cl + AsPhCl_2$ ; (4)  $AsPh_2Cl + AsCl_3 = 2AsPhCl_2$ ; (5)  $AsPhCl_2 + AsPh_3 = 2AsPh_2Cl$ . For these reactions with triphenylarsine a temperature approaching  $350^\circ$  is favourable. The products may be separated by any physical or chemical means, or should the diaryl compound be required as the main product, any monoaryl compound present in the reaction mixture may be converted by gently boiling with triphenylarsine, as expressed by reaction (5) above, and, conversely, should the mono-aryl compound be required, dry diaryl arsenious chloride present is transformed according to reaction (4).

G. F. M.

**Preparation of Aromatic Arsinic Acids.** ANTOINE MOUNEYRAT (Brit. Pat. 142947).—Aromatic arsinic acids are produced by the interaction of aromatic diazonium compounds with cold or warm aqueous or dilute alcoholic solutions of arsenious acid, in acid, neutral, or alkaline medium in the presence of a copper salt and a reducing agent adapted to the acid or alkaline medium employed. In acid medium, for example, hypophosphorous acid or cuprous hydroxide is suitable, whilst in neutral or alkaline medium, sodium hyposulphite, sodium formaldehydesulphoxylate, or even an excess of alkaline arsenite may be employed. The method of procedure is capable of numerous modifications in detail, of which examples are given. [See, further, *J. Soc. Chem. Ind.*, 1920, 527A.] G. F. M.

**Arsinic Acids Derived from Guaiacol and Veratrole.**  
**Constitution of the Polyarsenides.** ROBERT GEORGE FARGHER (T., 1920, 117, 865—875).

**A Sulphur Compound which is Present in Very Small Amounts in Salvarsan.** C. STRZYZOWSKI (*Korr.-Bl. Schweiz. Aerzte*, 47, 176; *Zentr. Biochem. Biophys.*, 1918, 19, 794. Compare Fargher and Pyman, T., 1920, 117, 372).—The author has detected in salvarsan a sulphur compound, which is possibly a sulpho-acid.

CHEMICAL ABSTRACTS.

**Sodium Compound of Diaminodihydroxyarsenobenzene Dihydrochloride.** U. SUZUKI (U.S. Pat. 1330288).—The dihydrochloride is moistened with ethyl alcohol and dissolved in methyl alcohol, and to the solution is added gradually a solution of sodium ethoxide or methoxide until a test portion gives a clear solution in a considerable excess of water. The whole liquid is added to ether containing 6—10% of ethyl alcohol, whereby the desired sodium compound is obtained as a yellowish-brown precipitate, which is washed with ether and dried in a vacuum. The whole process should be carried out in an atmosphere of hydrogen or nitrogen to prevent the possible formation of poisonous or deleterious substances, which may be produced in the presence of even small quantities of oxygen. The product contains 22—23% of arsenic, and its aqueous or physiological sodium chloride solution is suitable for injection.

CHEMICAL ABSTRACTS.

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### Physiological Chemistry.

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**The Analysis of the Carbon Dioxide Equilibrium in Blood According to H. Straub and K. Meyer.** LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1920, **103**, 53—59).—A critical discussion of the works of Straub and Meyer (A., 1918, ii, 467 ;

1919, i, 53; this vol., i, 200) on the combination of hæmoglobin with carbon dioxide. S. S. Z.

**The Catalase of the Erythrocytes.** H. VON EULER and E. BORGSTAM (*Biochem. Zeitsch.*, 1920, **102**, 124—131).—The catalase in the erythrocytes of horse's blood is activated by heat. At 57°, an increase in the activity amounting to 170% was observed. Chloroform and toluene activated the catalase only to a small extent. S. S. Z.

**Serum Lipochrome. I.** A. A. HIJMAN VAN DER BERGH and P. MULLER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 748—757).—Cow's serum was found to contain only carotene, and egg-yolk and fowl's serum only xanthophyll. Human serum usually contained both pigments, with a preponderance of carotene. These are similar observations to those recorded by Palmer (A., 1916, i, 186, 863). The authors do not, however, lend support to the suggestion advanced by the American workers that the lipochrome of cow's serum is present in the form of a complex with protein. Evidence is given that aqueous solutions of carotene, probably colloidal in nature, may be prepared, from which ether will not extract the pigment directly, but only after the addition of alcohol. Other reagents which affect the colloidal state will also "liberate" the carotene, so that it may be extracted by shaking with ether. Carotene in the two forms of solution may show different susceptibilities to destruction by light.

J. C. D.

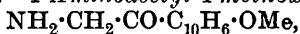
**Hæmolytic Action of some Chlorine Derivatives of Methane, Ethane, and Ethylene.** W. PLÖTZ (*Biochem. Zeitsch.*, 1920, **103**, 243—271).—Experiments with a number of chlorine derivatives of methane, ethane, and ethylene show that the hæmolytic activity of these compounds is proportional to their molecular weight and to the number of chlorine atoms. Stalagmometric experiments, on the other hand, have shown that there is no relation between the surface tension of these compounds and their hæmolytic activity. S. S. Z.

**A Thermostat with an Electromagnetic Regulator and Electrical Heating Apparatus.** G. JOACHIMOGLU (*Biochem. Zeitsch.*, 1920, **103**, 49—53).—A description of an arrangement of apparatus suitable for experiments with isolated mammalian organs. S. S. Z.

**Sympathomimetic Amines. I. Amino-derivatives of Naphthalene.** A. MADINAVEITIA (*Anal. Fis. Quim.*, 1920, **18**, 66—78).—The compounds described were prepared to ascertain whether the physiological action of bases related to adrenaline persists in compounds containing a naphthalene instead of a benzene nucleus and an amino-group in the side-chain in the  $\beta$ -position to the nucleus.  $\beta$ -Methoxy- $\alpha$ -naphthylethylmethyl-



amine,  $C_{10}H_7 \cdot CH(OMe) \cdot CH_2 \cdot NHMe$ . The corresponding  $\beta$ -methoxy- $\beta$ -phenylethylmethylamine,  $OMe \cdot CHPh \cdot CH_2 \cdot NHMe$ , b. p.  $105-106^\circ$  at 22 mm., was also prepared, as it had not been described previously. 1-Aminoacetyl-4-methoxynaphthalene,



has m. p.  $67^\circ$ .  $\alpha$ -Aminoacetylnaphthalene,  $NH_2 \cdot CH_2 \cdot CO \cdot C_{10}H_7$ , is described. Tests on the physiological action (constriction of blood vessels) were carried out with the compounds and with  $\beta$ -phenylethylmethylamine used as a standard. The tests proved that a naphthalene compound is forty times more active than a benzene one; that a methoxy-group does not materially affect the physiological properties; and that a carbonyl group in the side-chain decreases, but a hydroxyl group in the nucleus increases, the action of the compound on the blood pressure.

W. R. S.

## Chemistry of Vegetable Physiology and Agriculture.

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**Decomposition of *dl*-Phenylalanine by *Bacillus proteus* and *Bacillus subtilis*.** HAJIME AMATSU and MIDORI TSUDJI (*Acta Scholae Med. Univ. Imperial Kioto*, 1918, 2, 447—457).—Each micro-organism (*Bacillus proteus* and *B. subtilis*) was permitted to act in pure culture on a nutrient solution which contained inorganic salts, glycerol, *dl*-phenylalanine, and either a phosphate mixture or lactose plus freshly precipitated uranyl phosphate. Incubation occurred for forty days at 37°. Both bacterial species consumed the *dl*-phenylalanine to a marked degree; that which was recovered after the action of *B. proteus* was dextrorotatory; that which was recovered after the action of *B. subtilis* was optically inactive; apparently *B. proteus* acted asymmetrically, whilst *B. subtilis* attacked both antipodes. Both organisms formed phenyl-lactic acid and phenylethylamine. In the presence of lactose and uranyl phosphate, this amine was formed to a marked degree, but the acid could not be found in the culture. In the presence of a phosphate mixture, the acid was the chief product, and only a very small amount of the amine was formed. *B. proteus* produced *d*-phenyl-lactic acid, whilst *B. subtilis* made *l*-phenyl-lactic acid. CHEMICAL ABSTRACTS.

**Formation of Tyrosol from *l*-Tyrosine by Bacteria.** KINSABURO HIRAI (*Acta Scholae Med. Univ. Imperial Kioto*, 1918, 2, 425—432).—A strain of *Bacillus lactis aerogenes*, isolated from the faeces of a breast-fed infant, produced small amounts of tyrosol (*p*-hydroxyphenylethyl alcohol) from *l*-tyrosine during incubation for thirty to thirty-three days at 25° or 37°; none was formed at 45°. The yield was increased by addition of a phosphate mixture to the nutrient solution, which also contained uranyl phosphate

and either dextrose or lactose. Tyrosol was not obtained by the action of *B. lactis aerogenes* on tyramine hydrochloride. Another strain of this organism did not produce tyrosol from *l*-tyrosine.

CHEMICAL ABSTRACTS.

**The Chemical Composition of the Tubercle bacillus.**

A. GORIS (*Compt. rend.*, 1920, **170**, 1525—1527).—Tubercle bacilli when washed free from bouillon, dried at 37°, and extracted with chloroform yielded a substance precipitable from chloroform solution by ether, which the author names *hyalinol*, 7 grams being obtained from 1500 grams of dry bacilli. When saponified by sodium hydroxide, the sodium salts of crotonic and isocrotonic acids, and a small amount of a substance having an odour of jasmin and mimosa, are obtained.

W. G.

**Action of Different Acids on the Growth of Mucor.**

BETTINGER and DELAVAL (*Bull. Assoc. Chim. Sucr.*, 1920, **37**, 254—261).—The mucor employed for saccharification in distilleries is favourably affected in its vegetative growth by a slight addition of mineral or organic acid to the liquefied cereal mash. The optimum amount of acid varies in a general way inversely with the degree of ionisation, but acetic and succinic acids, which are excretion products, exert a disproportionately great inhibitive action when present in more than the optimum amounts, although their influence is very favourable to growth if this amount is not exceeded. [See also *J. Soc. Chem. Ind.*, 1920, 555A.] J. H. L.

**The Yeast *Saccharomyces thermantitonus*.**

HANS VON EULER and INGVAR LAURIN (*Biochem. Zeitsch.*, 1920, **102**, 258—268).—A strain of *Saccharomyces thermantitonus* emanating from the Institut für Gärungsgewerbe in Berlin was examined by the authors for its growth, fermentation, and inversion capacities. They found that the limits of temperature characteristic for this species have altered after fifteen years' cultivation in the laboratory on beer wort. A similar observation has been previously made by the authors on a strain of *S. thermantitonus* which came from Jörgensen's laboratory. It is therefore concluded that the yeast, during the years of cultivation in the laboratory, adapted itself to a lower temperature.

S. S. Z.

**Formation and Significance of Hexosediphosphoric Acid in the Metabolism of Yeast.**

CARL NEUBERG (*Biochem. Zeitsch.*, 1920, **103**, 320—336. Compare A., 1918, i, 91).—Fresh bottom yeast in the presence of toluene does not utilise inorganic phosphate, whilst the same yeast after drying esterifies the phosphates. The formation of hexosediphosphate, therefore, does not take place under normal conditions of alcoholic fermentation.

S. S. Z.

**Sulphurous Acid and Yeast Fermentation.**

ERIK HÄGGLUND (*Biochem. Zeitsch.*, 1920, **103**, 299—306).—0.007N-Sulphurous acid completely inhibited the fermentation of 1 gram

of yeast in 25 c.c. of solution. 0.005*N*-Acid did not completely inhibit its activity. The toxic effect of sulphurous acid on yeast fermentation is attributed to the undissociated acid. Sodium sulphite showed an inhibitive action as compared with potassium sulphate. A 0.2*N*-potassium sulphate solution increased the fermentation by about 25%. S. S. Z.

**Fermentation of Pyruvic Acid under the Conditions of the Fixation Method.** [Fermentation of Pyruvate-Sulphite by Yeast.] CARL NEUBERG and ELSA REINFURTH (*Ber.*, 1920, **53**, [B], 1039—1052).—In consequence of the doubts recently cast by Zerner (this vol., i, 350) on the validity of the authors' theory of the intermediate formation of acetaldehyde and pyruvic acid during the course of alcoholic fermentation, the behaviour of the pyruvic acid-sulphite complex has been further studied. It is found that, under greatly varied conditions, the complex is at least as readily fermented by yeast as is pyruvic acid itself. All types of yeast and yeast preparations decompose pyruvic acid in the presence of an equivalent or greater amount of soluble hydrogen sulphites. Under suitable conditions of permeability, which appear to be comparable with the osmotic requirements of sugar fermentation, the pyruvic acid-sulphite complex, in spite of its stability, is more readily fermented than the unstable sugar-sulphite compound. The individual experiments include the fermentation of pyruvic acid in the presence of normal sodium sulphite (1 mol.) by top and bottom yeast, of a molecular mixture of the acid and sulphur dioxide by dry top and bottom yeast, of the pyruvate-sulphite complex by the acetone preparations of either yeast, and by alcohol-ether yeast, of equivalent amounts of pyruvic acid and sodium sulphite by fresh toluolised yeast, and by yeast juice. The fermentation of calcium pyruvate-sulphite and of pyruvic acid in the presence of more than one molecular proportion of sodium sulphite has also been investigated. H. W.

**The Phytochemical Reduction of *o*-Nitrobenzaldehyde.** F. F. NORD (*Biochem. Zeitsch.*, 1920, **103**, 315—320).—Yeast reduces about 10% of *o*-nitrobenzaldehyde to *o*-nitrobenzyl alcohol. The aldehyde group is therefore reduced phytochemically more easily than the nitro-group. S. S. Z.

**The Regulator System: Primary Phosphate-Bicarbonate-Free Carbonic Acid, in place of the System: Primary Phosphate-Secondary Phosphate.** W. WINDISCH and W. DIETRICH (*Biochem. Zeitsch.*, 1920, **102**, 141—150).—See this vol., i, 352.

**The Velocity of the Photochemical Decomposition of Carbon Dioxide in Living Cells.** OTTO WARBURG (*Biochem. Zeitsch.*, 1920, **103**, 188—218).—When a cell which has been kept in the dark is exposed to intense light, the velocity of assimilation in it shows an initial lag before it becomes constant. This lag is

not observed if the cell is exposed to light of low intensity. On submitting the cell to darkness after exposure to intense light, the assimilation gradually ceases. The velocity of assimilation in the cell sinks as the pressure of oxygen increases from one-fiftieth to one atmosphere. The rate of inhibition of the narcotic phenylurethane on the cell is similar to that of the concentration of narcotics as expressed by Freundlich's adsorption curve, which suggests that it is a surface action. Hydrocyanic acid inhibits the photochemical emission of oxygen from carbon dioxide, but not from the intermediate products of respiration formed in the cell; it also inhibits the formation of respiratory carbon dioxide in the cell. Oxygen is split off from nitrates and nitric acid by a suspension of vegetable cells on exposure to light. The kinetics of the photolytic action of the cell in assimilation is discussed.

S. S. Z.

**The Presence of Copper in the Vegetable Organism.**

E. FLEURENT and LUCIEN LÉVI (*Bull. Soc. chim.*, 1920, [iv], **27**, 440—441).—The authors have extended their work on the presence of copper in plants (compare A., 1911, ii, 445), and have found it to be present in ten other species and to be situated particularly in the leaves.

W. G.

**The Presence of Copper in the Vegetable and Animal Organisms.** E. FLEURENT and LUCIEN LÉVI (*Bull. Soc. chim.*, 1920, [iv], **27**, 441—442. Compare preceding abstract).—The percentages of copper found in a number of plants, and also in certain animal products, such as milk, meat, and egg-yolk, are given.

W. G.

**A Case of Favourable Action of Copper on Vegetation.**

L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1920, **170**, 1542—1545).—Cases are reported where copper sulphate added to water-culture solution exerted a favourable action on the growth of roots and stems of pea and wheat plants during the nine days after germination, and on the root and leaf development of lettuce plants during the thirty-three days after germination. In the first case, 0.2 mg. of anhydrous copper sulphate per litre was used, and for the lettuce 0.02 mg. per litre gave the best results.

W. G.

**Plasmolysing Action of a Certain Number of Vapours.**

P. GUÉRIN and CH. LORMAND (*Compt. rend.*, 1920, **170**, 1598—1601. Compare Mirande, A., 1910, ii, 884).—The plasmolysis was indicated by the liberation of hydrogen cyanide from the young leaves of cherry laurel or the blackening of the leaves of *Aucuba japonica*. All the alcohols and aldehydes examined exerted a plasmolysing action, as did such substances as *p*-benzoquinone, pyridine, and dichlorobenzene. In certain cases in which Mirande (*loc. cit.*) obtained negative results, the authors have obtained decidedly positive results.

W. G.

**Colloid-chemical Researches on Plant Plasma.** TETSUTARO TADOKORO (*J. Coll. Agr. Hokkaido Imp. Univ., Sapporo, Japan*, 1919, 8, 143—182).—I. *Alteration of the colloidal properties of plasma by the addition of neutral salts.*—The press juice obtained by macerating wheat sprouts 5—8 cm. long with quartz sand was treated with increasing concentrations of various chlorides and with various salts of magnesium. After keeping a certain time, the sedimentation was compared with that of an untreated control. The results show, in general, flocculation by  $\text{AlCl}_3 > \text{BaCl}_2 > \text{SrCl}_2 > \text{CaCl}_2 > \text{MgCl}_2$ , and deflocculation by  $\text{KCl} > \text{NH}_4\text{Cl} > \text{NaCl}$ . Magnesium salts of 0.01*N*-concentration cause flocculation in the order  $\text{I} > \text{Cl} > \text{NO}_3 > \text{SO}_4 > \text{acetate}$ , but at 0.2*N*, whilst the iodide shows steadily increasing flocculation, the other cations show deflocculations in the following order:  $\text{SO}_4 > \text{NO}_3 > \text{acetate} > \text{Cl}$ . With 0.1*N*-calcium salts, flocculation occurs in the following order:  $\text{acetate} > \text{I} > \text{NO}_3 > \text{Cl}$ . Comparing these results with those of other investigators, it is found that salt concentrations which poison wheat also cause colloidal changes in the press juice. II. *Antagonism and the alteration of the plasma colloids.*—Experiments showing the antagonism between various salts in their action on press juice of wheat sprouts were paralleled by pot-culture experiments showing a corresponding effect of the same mixture on the growth of the wheat plant. The following pairs of salts were used:  $\text{NaCl}-\text{CaCl}_2$ ,  $\text{KCl}-\text{CaCl}_2$ ,  $\text{KCl}-\text{MgSO}_4$ ,  $\text{K}_2\text{SO}_4-\text{MgCl}_2$ ,  $\text{CaCl}_2-\text{MgCl}_2$ ,  $\text{CaCl}_2-\text{MgSO}_4$ . The essential basis of antagonism lies in the maintenance of a certain optimum degree of colloidal dispersion, which the author terms "life-colloidal." For example, sodium chloride tends to deflocculate and calcium chloride tends to flocculate, so that the proper balance between them maintains the optimum dispersion. In like manner, asparagine, glycine, and peptone produce flocculation of press juice in increasing order, whilst sucrose, dextrin, and dextrose produce deflocculation. Therefore, as experiments demonstrate, dextrose is antagonistic to calcium chloride, whereas glycine is antagonistic to potassium chloride. Two other series of experiments show that the same basis of antagonism extends to diffusion through the press juice of *Brassica* leaves, and to the effect of the salts, etc., on the enzymic action of wheat sprout amylase and taka-diastrase. CHEMICAL ABSTRACTS.

**A Quantitative Study of the Effect of Anions on the Permeability of Plant Cells.** ORAN L. RABER (*J. gen. Physiol.*, 1920, 2, 535—539).—The salts used were all sodium salts, the solutions having  $p_H = 7 \pm 0.5$ , and their effects on the permeability of *Laminaria agardhii*, Kjellm, were determined. When these salts were used in solutions having the same conductivity, the anions arranged themselves in the order  $\text{I}', \text{Br}', \text{CNS}', \text{Cl}', \text{NO}_3', \text{CH}_3\text{CO}_2', \text{SO}_4'', \text{C}_2\text{H}_4\text{O}_2(\text{CO}_2)_2'', \text{PO}_4''', \text{C}_3\text{H}_5\text{O}(\text{CO}_2)_3'''$  as regards their effect on the permeability, there being thus slight differences from Hofmeister's series. Where the salts were used in equimolecular solutions, the series became  $\text{CNS}', \text{I}', \text{Br}', \text{NO}_3', \text{Cl}'$ ,

$\text{CH}_3\cdot\text{CO}_2'$ ,  $\text{SO}_4''$ ,  $\text{C}_2\text{H}_4\text{O}_2(\text{CO}_2)_2''$ ,  $\text{PO}_4'''$ ,  $\text{C}_3\text{H}_5\text{O}(\text{CO}_2)_3''$ , the salts apparently forming themselves into two distinct groups. W. G.

**The Antagonistic Action of Anions.** ORAN L. RABER (*J. gen. Physiol.*, 1920, **2**, 541—544).—Distinct antagonism is shown between the acetate and sulphate anions when used as their sodium salts in their effect on the permeability of *Laminaria*. W. G.

**Presence in Melilotus and Asperula odorata of Glucosides yielding Coumarin under the Hydrolysing Action of Emulsin.** EM. BOURQUELOT and H. HÉRISSEY (*Compt. rend.*, 1920, **170**, 1545—1550).—Three species of *Melilotus* and *Asperula odorata* were all found to contain a glucoside, which, under the influence of emulsin, gave coumarin. It is probable that the glucoside which yields coumarin varies from one plant species to another. W. G.

**The Alkaloid Constituents of Rice Polishings.** FRANZ HOFMEISTER [with MASAHIKO TANAKA] (*Biochem. Zeitsch.*, 1920, **103**, 218—225).—The author has isolated from rice an alkaloid substance, *oridine*, which possessed anti-neuritic activity, but on purification, it became inactive. The hydrochloride was prepared as follows: Rice meal was extracted with 80% alcohol. The alcoholic extract was evaporated to a syrup in a vacuum, and made up with hydrochloric acid to a solution containing 3% of the acid. After extraction of impurities with ether, the acid solution was concentrated again to a syrup and made feebly alkaline with sodium carbonate, and precipitated with bismuth-potassium iodide solution. After acidifying the filtrate, the precipitation was repeated, and the precipitate was triturated with silver carbonate and decomposed with hydrochloric acid. The substance was then obtained in crystalline form on drying the filtrate. Doses of 5—10 mg. of the hydrochloride were found to be active. The *aurichloride*,  $\text{C}_5\text{H}_{11}\text{O}_2\text{N}\cdot\text{HAuCl}_4$ , formed platelets and flat prisms, m. p. 277°. *Oridine hydrochloride*,  $\text{C}_5\text{H}_{11}\text{O}_2\text{N}\cdot\text{HCl}$ , forms colourless prisms, m. p. 240°. The free base was a white, hygroscopic powder, soluble in water. It was found to be isomeric with betaine and valine, and, according to its properties, it is conjectured to be related to the pyridine and piperidine groups. S. S. Z.

**The Mosaic Disease of Spinach as Characterised by its Nitrogen Constituents.** S. L. JODIDI, S. C. MOULTON, and K. S. MARKLEY (*J. Amer. Chem. Soc.*, 1920, **42**, 1061—1070).—Previous work on the nitrogen metabolism of the spinach plant (*J. Agric. Research*, 1918, **15**, 372, 381, 385) had led to the assumption that denitrification takes place in the diseased plant. With the object of corroborating this, material from other fields and another year has been examined. It is thus shown that the mosaic disease is accompanied by a lower total, and also nitric, nitrogen content,

but a higher ammoniacal nitrogen content of the diseased leaf tissue. Further, nitrites are present in diseased but not in healthy leaves. Probably as a result of this, the basic (diamino-) and non-basic (monoamino-) nitrogen content of diseased leaf tissue is less than that of healthy tissue. The proportion of protein nitrogen and protein in healthy leaves is greater than in the roots, but in diseased material there is practically no difference, the actual percentages being greater in the latter case, with the exception that the leaves show a higher protein content in health than in disease. It is therefore concluded that denitrification of leaves, but not of roots, is characteristic of mosaic disease. J. K.

**The Unsaturated Alcohol of the Essential Oil of Freshly Fermented Tea Leaves.** P. VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 758—761).—The alcohol is  $\Delta^7$ -hexene- $\alpha$ -ol, identical with that obtained by Walbaum from Japanese oil of peppermint (A., 1918, i, 302). J. C. D.

**Action of Gaseous Chlorine and Bromine on Medicinal Plants.** DOMENICO LIOTTA (*Arch. Farm. sper. Sci. aff.*, 1919, **28**, 152—160, 161—169).—When treated with chlorine or bromine, the leaves of *Nerium oleander* and of *Digitalis purpurea* completely lose their toxic properties. Experiments made with the leaves of *Prunus laurocerasus* yielded no definite results, but the leaves employed were gathered in November, at which time they are almost devoid of amygdalin.

Similar tests were made with leaves of *Pilocarpus pinnatifolius*, *Arnica montana*, *Nicotiana tabacum*, *Atropa belladonna*, *Lobelia inflata*, and *Aconitum napellus*. In these cases, the aqueous extracts of the leaves are turbid and difficult to filter, but become limpid and easy to filter after the leaves have been treated with chlorine or bromine. In those cases where the aqueous extract causes death, the aqueous extract of the treated leaves produces the same effect.

With the former group, the halogen apparently produces hydrolysis of the glucoside present, whereas, with the latter, a salt of the alkaloid is probably formed. The action of chlorine or bromine may serve to decide whether the active principle of leaves is glucosidic or alkaloidal in character, and such treatment furnishes a simple means of extracting alkaloids from vegetable or animal substances. T. H. P.

**Acidity and Acidimetry of Soils. II. Investigation of Acid Soils by means of the Hydrogen Electrode.** HENRY G. KNIGHT (*J. Ind. Eng. Chem.*, 1920, **12**, 457—464. Compare this vol., i, 468).—A hydrogen electrode cell suitable for use in soil investigations is described, as are also the results of experiments on the rate of reactions between normal salt solutions and soils, the rate of reaction in the presence of a base, the change in hydrogen ion concentration with change of amount of base and



with time, and the change in conductivity of soil solutions. [See, further, *J. Soc. Chem. Ind.*, 1920, 523A.] W. P. S.

**Relative Absorption by Soil of Sodium Carbonate and Sodium Chloride.** THOMAS H. KEARNEY (*Soil Sci.*, 1920, **9**, 267—273).—Observations on plants growing in alkali soils have shown that sodium carbonate is more toxic than sodium chloride, whereas many laboratory experiments on the toxicity of added salts have given the reverse result. Experiments were made to determine whether this difference was due to differences in the amount of absorption of the salts by the soil producing soil solutions of very different concentrations. Solutions of sodium carbonate and sodium chloride of varying concentration were added to sand, and after leaving for twenty-four hours for absorption to become complete, the electrical resistance of the sand was determined by the bridge method. The results obtained showed that 63% of the sodium carbonate was absorbed from solution by the sand, whereas only 23% of the sodium chloride was absorbed.

J. H. J.

**The Absorbent Power of Soil with Respect to Manganese.** P. NOTTIN (*Compt. rend.*, 1920, **171**, 44—47).—Compost or turf absorbs manganese from solutions of manganous salts to a far greater extent than does ordinary soil. This the author attributes to a difference in the crystallographic state of the calcium carbonate present in the soil. He shows that calcite is not acted on by a 1% solution of manganous chloride, whilst aragonite or ktypeite is dissolved to a very large extent, and an appreciable amount of manganese is thrown out of solution.

W. G.

**Effect of Calcium Sulphate on the Solubility of Soils.** M. M. MCCOOL and C. E. MILLAR (*J. Agric. Res.*, 1920, **19**, 47—54).—Six soils of different types were treated with a saturated solution of calcium sulphate for twenty-four hours. In one series the soil was then simply drained on a filter, and in another series it was washed with distilled water until the amount of soluble material was reduced to a minimum. In both series, the rate of formation of soluble substances at high and low water content was then determined by the freezing-point method and compared with that for untreated soil. In every case, the treatment was found to have caused a very large increase in the rate of formation of soluble substances. Similar treatment with a *N*/10-solution of calcium phosphate, on the other hand, decreased the rate of formation of soluble substances, and when used with calcium sulphate, decreased its effect.

If the carbon dioxide produced may be taken as a measure of biological activities, the effects described above cannot be ascribed to increase in biological activity, but require some other explanation.

W. G.

## Organic Chemistry.

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### **The Origin of Petroleum. Formation from Free Fatty Acids or Soaps. Formation from Animal Hydrocarbons.**

AD. GRÜN and TH. WIRTH (*Ber.*, 1920, **53**, [B], 1301—1312).—A modification of Engler's theory of the origin of petroleum from fats has recently been put forward by Pictet and Potok (A., 1919, i, 569), who base their ideas on the experimental results obtained by the distillation of sodium stearate and sodium oleate under diminished pressure, whereby they claim to have isolated hydrocarbons of high molecular weight. The authors have attempted to repeat Pictet and Potok's experiments as far as is possible from the description given in the literature, and have obtained totally different results. Paraffins of high molecular weight are not obtained; the main products are liquid unsaturated hydrocarbons and pentatriacontanone, the latter of which is practically completely decomposed when the distillates are fractionated at the ordinary pressure.

The recent isolation of hydrocarbons by Mastbaum, Tsujimoto, and Chapman in considerable quantity from the liver oils of certain fish may possibly have an important bearing on the origin of petroleum. In favour of this hypothesis, it may be noted that these fish are most closely allied to those of past ages, that the animal hydrocarbons with branched chains contain asymmetric carbon atoms which may account for the optical activity of petroleum, and lastly that the conversion of complex hydrocarbons into naphthenes can be readily explained, since, for example, Chapman has found that spinacene yields a cyclic hydrocarbon when distilled over sodium.

H. W.

**Pyrogenic Acetylene Condensations. VI.** RICHARD MEYER and KURT TAEGER (*Ber.*, 1920, **53**, [B], 1261—1265).—Further examination of the mixture of picrates obtained from the fractions of higher boiling point derived from the acetylene tar described previously (A., 1919, i, 72) has shown the presence of fluorene, acenaphthene, anthracene, phenanthrene, pyrene, small quantities of fluoranthene, and a hydrocarbon,  $C_{17}H_{10}$ , m. p.  $186^{\circ}$ , which yields a picrate, m. p.  $231^{\circ}$ .

H. W.

**Catalytic Oxidation of Alcohols by the Use of Metallic Oxides and of Finely Divided Metals.** J. B. SENDERENS (*Ann. chim.*, 1920, [ix], **13**, 266—283).—The oxidation of alcohols under the catalytic influence of various powdered metallic oxides (nickel, copper, vanadium, molybdenum, zinc oxides) gave unsatisfactory results in so far as the production of aldehydes or acids is concerned.

Various metals were tried in the form of turnings or powder as

catalysts for this oxidation, but the only one which gave at all satisfactory results was silver.

W. G.

**The Phosphatides.** ERNEST FOURNEAU (*Bull. Soc. chim. Biol.*, 1920, **2**, 67—87).—A general discussion of these substances. It appears certain that ordinary "lecithin" is a mixture of true lecithin and kephalin.

J. C. D.

**Density and Coefficient of Expansion of  $\beta\beta'$ -Dichlorodiethyl Sulphide.** JOHN A. WILKINSON and CHRIS WERNLUND (*J. Amer. Chem. Soc.*, 1920, **42**, 1382—1385). The density and coefficient of expansion of dichlorodiethyl sulphide have been determined by the dilatometric method at temperatures between 15° and 90°. The density changes uniformly from 1.2790 at 15° to 1.1996 at 90°, the change being 0.001058 per degree. The coefficient of expansion is also uniform over this temperature range, and amounts to 0.000881 c.c. per degree.

J. F. S.

**Synthetic Notes [Alkyl Sulphuryl Chlorides.  $\alpha$ -Bromophenylacetonitrile.  $\alpha$ -Bromo- $\alpha$ -oximinoacetone and  $\alpha\alpha$ -Dichloro- $\alpha$ -nitrosoethane].** WILHELM STEINKOPF, WALTER MIEG, and JULIUS HEROLD (*Ber.*, 1920, **53**, [B], 1144—1148).—The methods of preparation (in part new and in part modifications of older processes) of various substances used by the authors in recent work are described.

*n*-Propylsulphuryl chloride,  $\text{OPr}\cdot\text{SO}_2\text{Cl}$ , b. p. 70—72°/20 mm. (slight decomp.), was on one occasion obtained by the action of sulphuryl chloride on *n*-propyl alcohol; attempts to repeat the preparation from other specimens of the reagents failed for some unexplained reason. *iso*Propyl and *iso*amyl alcohols are converted by sulphuryl chloride into the corresponding sulphuryl chlorides, but these cannot be distilled, and gradually decompose when preserved at the ordinary temperature. Ethylene chloro- and bromohydrins are almost quantitatively transformed by sulphuryl chloride into  $\omega$ -chloroethylsulphuryl chloride,  $\text{SO}_2\text{Cl}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ , b. p. 89—94°/water-pump vacuum, and  $\omega$ -bromoethylsulphuryl chloride, b. p. 100—105°/18 mm., respectively. Hydrogen chloride is evolved when sulphuryl chloride acts on ethyl glycollate, glycol monoacetate, and ethyl or methyl lactate, but the other products decompose when distilled or preserved at the ordinary temperature. Methylsulphuryl bromide could not be obtained from the corresponding chloride and hydrogen bromide, or from sodium methylsulphate and phosphorus pentabromide, or phosphorus and bromine. Methylsulphuryl chloride and potassium thiocyanate in acetone solution yield methyl thiocyanate,  $\text{SO}_2\text{Cl}\cdot\text{OMe} + \text{KCNS} = \text{MeSCN} + \text{SO}_2\text{Cl}\cdot\text{OK}$ . Phenol is exclusively chlorinated by sulphuryl chloride, yielding *o*-chlorophenol and, possibly, 2:4-dichlorophenol. The product obtained from phosphorus pentachloride and potassium phenyl sulphate has b. p. 143—145°/45 mm., and appears to be phenylphosphoryl dichloride,  $\text{OPh}\cdot\text{POCl}_2$ .

Phenylbromoacetonitrile is obtained as a yellow oil, b. p. 132—134°/12 mm., by the action of bromine vapour on phenylacetonitrile at 105° under the influence of powerful light. Tri-bromoacetyl bromide, b. p. 88—90°/12 mm., 210—215°/atmospheric pressure, is conveniently prepared from tribromoacetic acid and phosphorus tribromide.

Improved methods are given for the isolation of  $\alpha$ -bromo- $\alpha$ -oximinoacetone,  $\text{COMe}\cdot\text{CBr}\cdot\text{N}\cdot\text{OH}$ , m. p. 123—125°, and of  $\alpha\alpha$ -dichloro- $\alpha$ -nitrosoethane,  $\text{CH}_3\cdot\text{CCl}_2\cdot\text{NO}$ , b. p. 67—69°. H. W.

**The Chloro-derivatives of Methyl Formate and Methyl Carbonate.** V. GRIGNARD, G. RIVAT, and ED. URBAIN (*Ann. chim.*, 1920, [ix], **13**, 229—265).—A full account of work already published (this vol., i, 138, 139). W. G.

**The Successive Stages of the Hydrolysis of Triacetin.** EIICHI YAMASAKI (*J. Amer. Chem. Soc.*, 1920, **42**, 1455—1468).—It is shown that triacetin conforms to the statement that the hydrolysis of an ester formed by a polyhydric alcohol and a monobasic acid takes place according to the simple rule that each ester radicle has an equal rate of hydrolysis. Thus their rates are simply expressed in the same way as those of the successive reactions  $M_1 \rightarrow M_2 \rightarrow M_3 \rightarrow M_4$ , which have, respectively, the velocity constants  $3k$ ,  $2k$ ,  $k$ .  $M_1$  represents the triacetin,  $M_2$  the two isomeric diacetins,  $M_3$  the two isomeric monoacetins, and  $M_4$  glycerol. Detailed results of the hydrolysis of triacetin in 0.961*N*-hydrochloric acid at 35° are given. W. G.

**Chemical Nature of Margosic Acids (Fatty Acids of the Nim or Margosa Oil). Recent Conclusions Drawn from Experimental and Clinical Use of (Metallic) Margosates and Ethyl Margosate.** K. K. CHATTERJEE (*Indian Med. Gaz.*, 1919, **54**, 171—174).—The characteristic acid of this oil belongs to the linolic series, and is named *margosic acid* by the author, who suggests  $\text{C}_{22}\text{H}_{40}\text{O}_2$  for its formula. It forms about 23% of the total fatty acid present in nim oil. It is liquid at the ordinary temperature, yellow, and is optically inactive. Its sodium and potassium salts are soluble in water; its lead and barium salts are soluble in ether and light petroleum. The zinc, calcium, bismuth, mercury, and silver salts were also prepared. Ethyl margosate, prepared from the mixed fatty acids in this oil, is a clear, reddish-brown liquid having a fruity odour and a high b. p., and is more readily hydrolysed than potassium margosate. One c.c. of it injected intravenously gives rise to no harmful symptoms (in man). Post-mortem findings in a rabbit killed by injecting this compound showed that death was due to asphyxia. The author has treated several cases of leprosy, syphilis, and skin diseases by injecting the ester, sodium, and potassium salts of this acid with marked success.

CHEMICAL ABSTRACTS.

**Bromination of Glutaconic Acid and its Diethyl Ester.**

P. E. VERKADE and J. COOPS, jun. (*Rec. trav. chim.*, 1920, **39**, 586—593).—By exposing dry powdered glutaconic acid in a thin layer to the action of bromine vapour for seventy-two hours, the authors have obtained  $\alpha\beta$ -dibromoglutaric acid, m. p. 157°, without the formation of any hydrogen bromide. This acid, when debrominated by means of zinc and dilute sulphuric acid, gave only glutaconic acid. The authors consider that the  $\alpha\beta$ -dibromoglutaric acid obtained is the *trans*-form.

When ethyl glutaconate was brominated, even with the utmost precautions, there was always some hydrogen bromide formed. The ester obtained was not pure, but was in all probability the  $\alpha\beta$ -dibromoglutarate. When debrominated, the only product it yielded was glutaconic acid.

W. G.

**Relations between the Configuration and the Optical Rotatory Power of some Derivatives of Acids of the Sugar Group.** (MLLE) TH. W. J. VAN MARLE (*Rec. trav. chim.*, 1920, **39**, 549—572):—

With the view of seeing whether Hudson's rule (A., 1917, i, 318), as to the relationship between the direction of rotation and the configuration of the phenylhydrazides of the monobasic acids of the sugar groups, is applicable to other derivatives of such acids, the author has prepared a number of derivatives described below.

*d*-Gluconic acid gives a hydrazide, m. p. 142°,  $[\alpha]_D^{25} + 30.4^\circ$  (in water),  $[\alpha]_D^{14} + 20.9^\circ$  (in pyridine), yielding a benzylidene derivative, m. p. 157°,  $[\alpha]_D^{17} + 46.6^\circ$  (in pyridine), and a *p*-methoxybenzylidene derivative, m. p. 185°,  $[\alpha]_D^{15} + 54.0^\circ$  in pyridine; a *p*-bromophenylhydrazide, m. p. 203°,  $[\alpha]_D^{10} + 3.6^\circ$  (in water),  $[\alpha]_D^{15} - 15.3^\circ$  (in pyridine); a *p*-tolylhydrazide, m. p. 204°,  $[\alpha]_D^{15} + 5.0^\circ$  (in water),  $[\alpha]_D^{24} + 2.0^\circ$  (in pyridine); an *o*-tolylhydrazide, m. p. 218°,  $[\alpha]_D^{22} + 13.7^\circ$  (in water),  $[\alpha]_D^{17} + 5.1^\circ$  (in pyridine); a *m*-tolylhydrazide, m. p. 185°,  $[\alpha]_D^{16} + 4.5^\circ$  (in water),  $[\alpha]_D^{14} + 2.7^\circ$  (in pyridine); an *anilide*, m. p. 171°,  $[\alpha]_D^{11} + 50.6^\circ$  (in water); a *p*-toluidide, m. p. 181°,  $[\alpha]_D^{14} + 50.9^\circ$  (in water).

*d*-Mannonic acid gives a hydrazide, m. p. 161°,  $[\alpha]_D^{15} - 3.0^\circ$  (in water),  $[\alpha]_D^{14} - 38.8^\circ$  (in pyridine), yielding a benzylidene derivative, m. p. 194°,  $[\alpha]_D^{13} - 8.0^\circ$  (in pyridine), and a *p*-methoxybenzylidene derivative, m. p. 191°,  $[\alpha]_D^{15} - 18.8^\circ$  (in pyridine); a *p*-bromophenylhydrazide, m. p. 225°,  $[\alpha]_D^{10} - 7.3^\circ$  (in water),  $[\alpha]_D^{10} - 24.9^\circ$  (in pyridine); a *p*-tolylhydrazide, m. p. 208°,  $[\alpha]_D^{16} - 10.9^\circ$  (in water),  $[\alpha]_D^{14} - 24.8^\circ$  (in pyridine); an *o*-tolylhydrazide, m. p. 208°,  $[\alpha]_D^{15} - 8.7^\circ$  (in water),  $[\alpha]_D^{14} - 28.6^\circ$  (in pyridine), a *m*-tolylhydrazide, m. p. 214°,  $[\alpha]_D^{22} - 12.5^\circ$  (in water),  $[\alpha]_D^{14} - 24.7^\circ$  (in pyridine).

*d*-Galactonic acid gives a hydrazide, m. p. 178°,  $[\alpha]_D^{13} + 40.1^\circ$  (in water),  $[\alpha]_D^{14} + 31.1^\circ$  (in pyridine), yielding a benzylidene derivative, m. p. 193°,  $[\alpha]_D^{18} + 63.4^\circ$  (in pyridine), and a *p*-methoxybenzylidene derivative, m. p. 191°,  $[\alpha]_D^{16} + 67.7^\circ$  (in pyridine); a *p*-bromophenylhydrazide, m. p. 125°,  $[\alpha]_D^{18} + 2.5^\circ$  (in water),  $[\alpha]_D^{10} - 30.3^\circ$  (in pyridine);

a *p*-tolylhydrazide, m. p.  $212^{\circ}$ ,  $[\alpha]_D^{25} + 2.9^{\circ}$  (in water),  $[\alpha]_D^{14} - 13.5^{\circ}$  (in pyridine); an *o*-tolylhydrazide, m. p.  $191^{\circ}$ ,  $[\alpha]_D^{25} + 12.2^{\circ}$  (in water),  $[\alpha]_D^{10} - 8.6^{\circ}$  (in pyridine); a *m*-tolylhydrazide, m. p.  $174^{\circ}$ ,  $[\alpha]_D^{13} + 0.8^{\circ}$  (in water),  $[\alpha]_D^{14} - 15.8^{\circ}$  (in pyridine); an anilide, m. p.  $210^{\circ}$ ,  $[\alpha]_D^{17} + 62.6^{\circ}$  (in water); a *p*-toluidide, m. p.  $224^{\circ}$ ,  $[\alpha]_D^{16} + 72.9^{\circ}$  (in water); an *o*-toluidide, m. p.  $204^{\circ}$ ,  $[\alpha]_D^{11} + 49.9^{\circ}$  (in water); a *m*-toluidide, m. p.  $212^{\circ}$ ,  $[\alpha]_D^{14.5} + 63.3^{\circ}$  (in water).

*l*-Gulonic acid gives a hydrazide, a syrup,  $[\alpha]_D^{12} + 4.3^{\circ}$  (in water), yielding a benzylidene derivative, m. p.  $173^{\circ}$ ,  $[\alpha]_D^{17} - 11.2^{\circ}$  (in pyridine), and a *p*-methoxybenzylidene derivative, m. p.  $176-177^{\circ}$ ,  $[\alpha]_D^{14} - 2.9^{\circ}$  (in pyridine), a *p*-bromophenylhydrazide, and a *p*-tolylhydrazide, neither of which could be obtained pure.

*l*-Idonic acid gives a hydrazide, a syrup,  $[\alpha]_D^{15} - 21.8^{\circ}$  (in water), yielding a benzylidene derivative, m. p.  $153^{\circ}$ ; and a *p*-tolylhydrazide, which was not obtained pure.

*iso*Saccharic acid gives a hydrazide, a syrup,  $[\alpha]_D^{12} - 11.6^{\circ}$  (in water), yielding a benzylidene derivative, m. p.  $147^{\circ}$ ,  $[\alpha]_D^{17} - 48.2^{\circ}$  (in pyridine), and a *p*-methoxybenzylidene derivative, m. p.  $138^{\circ}$ ,  $[\alpha]_D^{14} - 36.2^{\circ}$  (in pyridine).

*l*-Arabonic acid gives a hydrazide, m. p.  $138^{\circ}$ ,  $[\alpha]_D^{12} + 52.6^{\circ}$  (in water),  $[\alpha]_D^{14} + 61.8^{\circ}$  (in pyridine), yielding a benzylidene derivative, m. p.  $208^{\circ}$ ,  $[\alpha]_D^{17} + 81.3^{\circ}$  (in pyridine), and a *p*-methoxybenzylidene derivative, m. p.  $208^{\circ}$ ,  $[\alpha]_D^{17} + 81.7^{\circ}$  (in pyridine); a *p*-bromophenylhydrazide, m. p.  $204^{\circ}$  (decomp.),  $[\alpha]_D^{17} + 2.4^{\circ}$  (in water),  $[\alpha]_D^{10} - 19.0^{\circ}$  (in pyridine); a *p*-tolylhydrazide, m. p.  $216^{\circ}$ ,  $[\alpha]_D^{17} + 4.08^{\circ}$  (in water),  $[\alpha]_D^{14} - 3.1^{\circ}$  (in pyridine); an *o*-tolylhydrazide, m. p.  $203^{\circ}$ ,  $[\alpha]_D^{18} + 26.6^{\circ}$  (in water),  $[\alpha]_D^{14} - 1.4^{\circ}$  (in pyridine); a *m*-tolylhydrazide, m. p.  $185^{\circ}$  (decomp.),  $[\alpha]_D^{15} + 4.6^{\circ}$  (in water),  $[\alpha]_D^{14} - 5.0^{\circ}$  (in pyridine); an anilide, m. p.  $204^{\circ}$ ,  $[\alpha]_D^{20} + 68.1^{\circ}$  (in water); a *p*-toluidide, m. p.  $200^{\circ}$ ,  $[\alpha]_D^{17} + 68.2^{\circ}$  (in water); an *o*-toluidide, m. p.  $172^{\circ}$ ,  $[\alpha]_D^{11} + 56.5^{\circ}$  (in water), and a *m*-toluidide, m. p.  $186^{\circ}$ ,  $[\alpha]_D^{11} + 67.7^{\circ}$  (in water).

*d*-Ribonic acid gives a hydrazide, m. p.  $150^{\circ}$ ,  $[\alpha]_D^{15} + 27.5^{\circ}$  (in water), yielding a benzylidene derivative, m. p.  $138-142^{\circ}$ , and a *p*-bromophenylhydrazide, m. p.  $169^{\circ}$ ,  $[\alpha]_D^{16} + 3.8^{\circ}$  (in water),  $[\alpha]_D^{10} + 14.0^{\circ}$  (in pyridine).

*l*-Xylonic acid gives a hydrazide, a syrup,  $[\alpha]_D^{15} + 34.5^{\circ}$  (in water), yielding a benzylidene derivative, m. p.  $153-155^{\circ}$ .

*d*-Lyxonic acid gives a hydrazide, m. p.  $188^{\circ}$ ,  $[\alpha]_D^{14} - 3.6^{\circ}$  (in water), which yields a benzylidene derivative, m. p.  $175^{\circ}$  (decomp.).

The results indicate that Hudson's law (*loc. cit.*) holds equally for the hydrazides, *p*-bromophenylhydrazides, *o*-, *m*-, and *p*-tolylhydrazides, amides, anilides, and *o*-, *m*-, and *p*-toluidides, the rule being applicable for aqueous solutions, but not for solutions in pyridine. The introduction of a phenyl or tolyl radicle into the amide group results in a considerable rise in the rotatory power. Of the three isomeric toluidides, the *para* invariably has the greatest rotation and the *ortho* the least.

Usually the *p*-methoxybenzylidene derivatives had a higher rotatory power than the corresponding benzylidene derivatives.

W. G.

**Ring Closure with Polycarboxylic Acids. I. The Dianhydride of Ethanetetracarboxylic Acid.** ERNST PHILIPPI and JULIE HANUSCH (*Ber.*, 1920, **53**, [B], 1300—1301).—*Ethane-*

*tetracarboxylic anhydride*,  $O \begin{array}{c} \diagup \text{CO} \cdot \text{CH} \cdot \text{CO} \diagdown \\ \diagdown \text{CO} \cdot \text{CH} \cdot \text{CO} \diagup \end{array} O$ , colourless needles,

which become discoloured at about 150° and decompose without melting at a higher temperature, is prepared by the action of warm acetic anhydride on ethanetetracarboxylic acid; the latter substance is re-formed by the action of water on the anhydride.

H. W.

**Improved Catalyst for the Manufacture of Acetaldehyde from Acetylene as the Primary Material, and Process for the Regeneration of the Catalyst.** SOCIÉTÉ DES ACIERIES ET FORGES DE FIRMINY (Brit. Pat. 124194).—An improved catalyst

for the hydration of acetylene consists of a solution of sulphuric acid containing mercury, ferric, and vanadium salts, which, after becoming exhausted, can be regenerated by electrolytic oxidation either intermittently or continuously, using a cell with a magnetite or platinum anode and a current density of 3—5 amperes per sq. cm., the temperature being maintained at 30—40°. By way of example, the catalyst may consist of 10—20% sulphuric acid containing in solution 2% of mercury, 0.3—0.5% of iron, and 0.025—0.1% of vanadium, the metals being present as sulphates. The optimum temperature of the bath for the conversion of acetylene into acetaldehyde is about 65°.

G. F. M.

**The Alleged Inactivation of *d*-Mannitol.** MASTA EHRLICH (*Biochem. Zeitsch.*, 1920, **103**, 312—315).—The author confirms Grün's observation that by dissolving the alkaline earth salts in a mannitol solution, a product is obtained which shows no rotation. Unlike Grün, however, she finds that when the strontium nitrate-mannitol solution is precipitated with acetone, as described by Grün, the mannitol thus obtained is identical with the active mannitol originally used. The mannitol is therefore not inactivated by this treatment, as is alleged by Grün.

S. S. Z.

**Glucosan.** AMÉ PICTET and PIERRE CASTAN (*Compt. rend.*, 1920, **171**, 243—245).—Gélis obtained a brown, amorphous substance, which he named glucosan, by heating dextrose at 170° (compare *ibid.*, 1860, **51**, 331). This compound can be obtained in a pure, crystalline state if the dextrose is heated at 150—155° under a pressure of 15 mm. So obtained, it has m. p. 108—109°, is very deliquescent, and has  $[\alpha]_D + 69.8^\circ$  in water. It reduces Fehling's solution, and when boiled with water gives dextrose again. When dissolved in methyl alcohol saturated with ammonia, it gives a crystalline compound, which is not glucosamine or isoglucosamine. When dissolved in methyl alcohol saturated with hydrogen chloride it gives  $\alpha$ -methyl glucoside. It yields a *tribenzoyl* derivative and a crystalline *bisulphite* compound. When dissolved in methyl alcohol and mixed with a solution of sodium methoxide in the same solvent, it gives a white *sodium* derivative, which, when

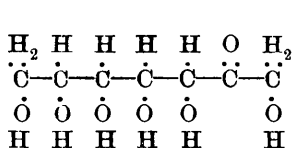
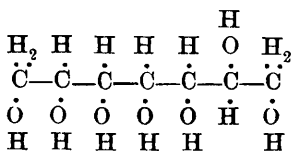
decomposed by dilute sulphuric acid, ultimately gives a methyl glucose. From its general behaviour the authors assign to glucosan the constitution

$$O \begin{array}{c} \text{CH} - \text{CH} \cdot \text{OH} \\ | \\ \text{CH} \cdot \text{O} \cdot \text{CH} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH} \end{array}$$

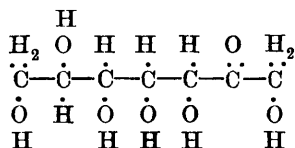
W. G.

### Sedoheptose, a New Sugar from *Sedum Spectabile*. II.

F. B. LA FORGE (*J. Biol. Chem.*, 1920, **42**, 367—374. Compare A., 1917, i, 444).— $\alpha$ -Sedoheptitol on oxidation with nitric acid gives pentahydroxypimelic acid. Of the ten theoretically possible heptitols, six are optically active, and of these six, five are known.  $\alpha$ -Sedoheptitol does not correspond with any of these five, and its constitution must therefore be given by the annexed formula. In the same way, considering the properties of inactive  $\beta$ -sedoheptitol and the constitution of the four possible inactive heptitols, of which only one is known, and since the  $\alpha$ - and  $\beta$ -sedoheptitols differ only in having the position of one hydroxyl group reversed, there are only two possible configurations for an  $\alpha$ -ketoheptose which will give such



(I.)



(II.)

heptitols, namely, formulæ I and II. At present it is not possible to distinguish between these two formulæ.

W. G.

### Volemitol. F. B. LA FORGE (*J. Biol. Chem.*, 1920, **42**, 375—376).

— $\alpha$ -Sedoheptitol gives an acetal, m. p. 191—194°, which is identical with that from the natural heptitol, volemitol, and it is now shown that these two heptitols are identical. The m. p. for tri-benzylidenevolemitol given by Bougault and Allard (A., 1903, i, 62) is erroneous.

W. G.

### Optical Properties of a Series of Heptitols. EDGAR T.

WHERRY (*J. Biol. Chem.*, 1920, **42**, 377—382).—The following are the refractive indices and densities of the eight known heptitols:

	$n_D^{20}$	$n_D^{25}$	$n_D^{30}$	D.
$\alpha$ -Mannoheptitol .....	1.538	1.545	1.549	1.485
$\beta$ -Mannoheptitol .....	1.533	?	1.545	1.470
$\alpha$ -Glucoheptitol .....	1.548	1.550	1.558	1.520
$\beta$ -Glucoheptitol .....	1.542	1.550	1.552	1.510
$\alpha$ -Sedoheptitol .....	1.550	1.555	1.562	1.520
$\beta$ -Sedoheptitol .....	1.564	1.570	1.584	1.590
$\alpha$ -Guloheptitol .....	1.554	1.560	1.570	1.560
$\beta$ -Guloheptitol .....	1.565	1.570	1.586	1.585

W. G.



**The Acidic and Basic Properties of Different Compounds.**

H. I. WATERMAN and J. GROOT (*Rec. trav. chim.*, 1920, **39**, 573—577).—In continuation of previous work (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, January), it is shown that the three cresols and *o*- and *m*-cresotic acids do not influence the hydrolysis of sucrose by hydrochloric acid, but that they all considerably retard the decomposition of dextrose by dilute aqueous sodium hydroxide. W. G.

**Physicochemical Investigations of the Diastatic Inversion of Sucrose.** ANDRÉE CHAUDUN (*Ann. chim.*, 1920, [ix], **13**, 301—349).—A more detailed account of work already published (compare A., 1918, i, 414; ii, 357; 1919, ii, 327; this vol., ii, 24).

W. G.

**Humic Acid.** F. FUCHS (*Chem. Zeit.*, 1920, **44**, 551).—Humic acid prepared from peat by the action of alkalis was found to be a true acid, and not a colloidal substance. It formed only simple salts, had a molecular weight of about 680, and contained 57.4% C, 4.6% H, and less than 1% of N and S. The salts of calcium, barium, magnesium, aluminium, copper, and iron were prepared. The silver salt was of variable composition (5 to 50% of silver). The humic acid was precipitated by both inorganic and organic acids. As stated by Albert (A., 1909, ii, 446), it dissolved as lithium humate when treated with lithium phosphate, which was decomposed in the reaction into the monohydrogen phosphate and hydroxide. Alkali humates are precipitated by sodium chloride solution, with the exception of a small residue, which can only be precipitated by acids, and when dried is soluble in sodium carbonate solution, whereas the portion precipitated by sodium chloride is much darker in colour, and when dried does not dissolve in sodium carbonate solution. On treating humic acid with sodium sulphide or sulphite, it yields a soluble sulphite compound, which reacts with aniline and other organic bases. C. A. M.

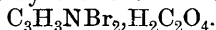
**New Derivatives of  $\beta\gamma$ -Dibromo- $\alpha$ -aminopropane and a New Base,  $C_3H_3N$ .** EMIL ABDERHALDEN and MAX PAQUIN (*Ber.*, 1920, **53**, [B], 1125—1143).—A series of products is described which originates in the spontaneous decomposition of solutions of  $\beta\gamma$ -dibromo- $\alpha$ -aminopropane in ether. In general, the constitution of the substances has not been elucidated definitely, but a preliminary account is now given.

When a solution of  $\beta\gamma$ -dibromo- $\alpha$ -aminopropane in dry ether is allowed to remain at slightly elevated temperature for two to four days, well-defined, prismatic crystals of the substance,  $C_3H_3NBr_2 \cdot HBr$ , m. p.  $164^\circ$ , separate. The success of the experiment depends largely on the dryness of the ether, since the presence of traces of moisture causes the separation of a yellow, amorphous substance (see later), which is only separated with great difficulty from the hydrobromide. The latter is obtained in a purer condition, m. p.  $170^\circ$ , from the hydrobromide of the base,

$C_6H_5NBr_2$  (see later), and is probably identical with the compound obtained in a similar manner by Paal from  $\beta$ -bromoallylamine. The free base,  $C_3H_3NBr_2$ , could not be isolated in the pure condition, since it is not volatile without decomposition, but the following salts are described: *nitrate*, pearly leaflets, m. p.  $76^\circ$  (incipient decomp.); *sulphate*,  $(C_3H_3NBr_2)_2H_2SO_4$ , crystalline powder, m. p.  $195^\circ$  (incipient decomp.); *formate*, pearly leaflets, m. p.  $105^\circ$  (slight decomp.); *oxalate*,  $C_3H_3NBr_2 \cdot H_2C_2O_4$ , m. p.  $173^\circ$  (decomp.); *picrate*, yellow needles, m. p.  $169^\circ$  (slight decomp.). The base appears to be a secondary amine; it does not give the carbylamine reaction or yield a precipitate with metaphosphoric acid. It gives a *benzoyl* derivative, m. p.  $130^\circ$ , a *benzenesulphonyl* compound, m. p.  $85^\circ$ , a *monomethyl* derivative [*hydrobromide*, slender needles, m. p.  $188^\circ$  (decomp.)], and a *compound*,  $C_{10}H_7NBr_2S_4$ , m. p.  $161^\circ$  (incipient decomp.), with carbon disulphide. The constitution  $HC \begin{smallmatrix} \text{CBr} \\ \text{NH} \end{smallmatrix} CHBr$  is suggested for the base. It readily reacts with hydrogen in alcoholic solution in the presence of colloidal palladium, yielding the pure hydrobromide,  $C_3H_3NBr_2 \cdot HBr$ , but the fate of the remainder of the molecule could not be established.

The yellow, amorphous substance,  $(C_3H_3NBr)_2$  (see above), darkens at about  $175^\circ$  and slowly melts and decomposes between  $250^\circ$  and  $260^\circ$ ; it is readily oxidised by bromine, without, however, yielding a product which is itself isolable in the pure state or yields pure salts.

An ethereal solution of the base,  $C_3H_3NBr_2$ , loses bromine when treated with sodium, and yields the base,  $C_3H_3N$ , which cannot be distilled without decomposition. Its salts with inorganic acids are extremely hygroscopic, whilst the compounds with organic acids are not generally well defined. It yields, however, an *oxalate*,  $C_3H_3N \cdot H_2C_2O_4$ , m. p.  $127^\circ$ , a *picrate*, needles, m. p.  $141^\circ$  (incipient decomp.), and a *compound* with mandelic acid,  $C_{10}H_7O_3N$ , m. p.  $124^\circ$ . Its close relationship to the parent base is proved by the conversion of its oxalate by bromine into the oxalate,

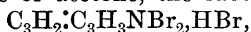


The constitution of the base is somewhat uncertain, since it does not give the reactions characteristic of secondary or tertiary amines, but the formula  $CH \begin{smallmatrix} \text{CH} \\ \text{N} \end{smallmatrix} CH$  appears most probable.

Although highly unsaturated, neither the base itself nor its salts can be hydrogenated in the presence of platinum or palladium under widely varied conditions.

Dehalogenation of the hydrobromide of the base,  $C_3H_3NBr_2$ , can be partly effected with alcoholic sodium ethoxide or with silver nitrate and nitric acid, but in this case a monobromo-derivative remains, which has not been further investigated.

When ethereal solutions of dibromoaminopropane are allowed to remain in the presence of acetone, the substances



m. p.  $198^{\circ}$  (decomp.), and  $C_9H_8NBr_2 \cdot HBr$ , m. p.  $168^{\circ}$  (decomp.), are obtained. The former is reconverted into the hydrobromide,  $C_3H_3NBr_2 \cdot HBr$ , when the ethereal solution of the liberated base is treated with bromine or simply preserved, or when the aqueous solution of the salt is acted on by excess of bromine. The *formate*,  $C_3H_2 : C_3H_3NBr_2 \cdot H \cdot CO_2H$ , has m. p.  $167^{\circ}$  (decomp.). The hydrobromide of the base,  $C_9H_8NBr_2$ , can be converted into an *oxalate*,  $C_9H_8NBr_2 \cdot H_2C_2O_4$ , m. p.  $116^{\circ}$  (decomp.), and a *nitrate*, m. p.  $105^{\circ}$  (incipient decomp.). The hydrobromide cannot be converted by oxidative degradation into the substance,  $C_3H_3NBr_2 \cdot HBr$ , nor can it be obtained from the latter or from  $C_6H_5NBr_2 \cdot HBr$  by the action of acetone. An ethereal solution of the free base deposits crystals of the hydrobromide in the course of a few days. The base may be dehalogenated by the action of sodium on its ethereal solution, but the corresponding bromine-free compound is decomposed with extraordinary readiness on exposure to air; it gives characteristic *compounds* with mercuric chloride, decomposing without melting at  $100^{\circ}$ , with picric acid, darkening at  $150^{\circ}$ , but not melting below  $250^{\circ}$ , and with salicylic acid, not melting below  $350^{\circ}$ .

H. W.

**Optically Active Iridium Compounds.** A. WERNER and AL. P. SMIRNOFF (*Helv. Chim. Acta*, 1920, **3**, 472—486).—The authors have prepared compounds belonging to two new complex iridium series, and have succeeded in resolving them into their optically active components, confirmation being obtained of Delépine's proof that co-ordinated saturated iridium complexes possess an octahedral spacial configuration (A., 1914, i, 1048). The action of ethylenediamine on hexahalogenated compounds of quadrivalent iridium yields only dark, uncrystallisable syrups, but from ethylenediamine and complexes containing either several nitro-groups or ammonia united to a trivalent iridium atom, complexes containing two or three molecules of the diamine are readily obtained. The salts thus prepared belong to the dinitrodiethylenediamineiridium and the triethylenediamineiridium series, and are colourless and highly stable, those of the former series being soluble only slightly, and those of the latter about ten times as soluble. The nitro-groups of the first series are so firmly united to the metallic atom that it is necessary to heat the compounds for some hours with concentrated sulphuric acid before nitrous acid is split off; with concentrated sulphuric acid and diphenylamine, the salts of this series give, not the ordinary blue, but a bright red, coloration, which is produced by the sulphuric acid alone. The new series closely resemble, and give the same precipitation reactions as, the dinitrotetrammineiridium series (compare Werner and de Vries, A., 1909, ii, 151) and the hexammineiridium series (compare Palmaer, A., 1896, ii, 179). Although two dinitro-series are possible theoretically, only one has been obtained, and as the  $\alpha$ -camphorsulphonates are separable into their optically active components, the compounds are of the *cis*- or 1:2-dinitrodiethylene-

diamineiridium series; this separation is readily effected with the help of nitrocamphor. The rotatory power of the triethylenediamine series is greater than that of the dinitro-series, and of about the same order of magnitude as those of the analogous rhodium and platinum compounds (compare Werner, A., 1912, i, 418). In the visible part of the spectrum both series exhibit normal rotatory dispersion.

The two series of compounds were prepared by the action of ethylenediamine monohydrate on sodium dichlorotetranitroiridate in a sealed tube at  $170^{\circ}$ , and were separated as iodides.

Salts of the racemic dinitrodiethylenediamineiridium series, 1:2- $[(\text{NO}_2)_2\text{Ir en}_2]\text{X}$ , the *iodide*, *bromide*, *nitrate*, *perchlorate*, and *d-(\alpha-bromo)-\pi*-camphorsulphonate, 1:2- $[(\text{NO}_2)_2\text{Ir en}_2]d\text{-C}_{10}\text{H}_{14}\text{O}_4\text{BrS}$ , were prepared.

Salts of the *d*-dinitrodiethylenediamineiridium series: *d-camphorsulphonate*,  $d-[(\text{NO}_2)_2\text{Ir en}_2]d\text{-C}_{10}\text{H}_{15}\text{O}_4\text{S}$ ; *bromide*, colourless, shining polyhedra,  $[\alpha]_C + 17.2^{\circ}$ ,  $[\alpha]_D + 26^{\circ}$ ,  $[\alpha]_E + 40^{\circ}$ ; *perchlorate*, white, crystalline powder,  $[\alpha]_C + 16.4^{\circ}$ ,  $[\alpha]_D + 24.8^{\circ}$ ,  $[\alpha]_E + 38.4^{\circ}$ ; *nitrate*, flat, shining needles,  $[\alpha]_C + 18^{\circ}$ ,  $[\alpha]_D + 27.2^{\circ}$ ,  $[\alpha]_E + 41.2^{\circ}$ .

Salts of the *l*-dinitrodiethylenediamineiridium series: *l-camphorsulphonate*,  $l-[(\text{NO}_2)_2\text{Ir en}_2]l\text{-C}_{10}\text{H}_{15}\text{O}_4\text{S}$ ; *bromide*,  $[\alpha]_C - 17.6^{\circ}$ ,  $[\alpha]_D - 26^{\circ}$ ,  $[\alpha]_E - 40^{\circ}$ ; *perchlorate*,  $[\alpha]_C - 16.8^{\circ}$ ,  $[\alpha]_D - 25.6^{\circ}$ ,  $[\alpha]_E - 39.2^{\circ}$ ; *nitrate*,  $[\alpha]_C - 17.6^{\circ}$ ,  $[\alpha]_D - 26.8^{\circ}$ ,  $[\alpha]_E - 41.6^{\circ}$ .

Salts of the racemic triethylenediamineiridium series,  $[\text{Ir en}_3]\text{X}_3$ : *bromide* ( $+ 3\text{H}_2\text{O}$ ), *nitrate*, and *perchlorate*.

Salts of the *d*-triethylenediamineiridium series: *iodide*,  $[\alpha]_C + 30^{\circ}$ ,  $[\alpha]_D + 42^{\circ}$ ,  $[\alpha]_E + 56^{\circ}$ ; *nitrate*,  $[\alpha]_C + 41.2^{\circ}$ ,  $[\alpha]_D + 57.2^{\circ}$ ,  $[\alpha]_E + 75.2^{\circ}$ ; *perchlorate*,  $[\alpha]_C + 34.5^{\circ}$ ,  $[\alpha]_D + 48.5^{\circ}$ ,  $[\alpha]_E + 64^{\circ}$ .

Salts of the *l*-triethylenediamineiridium series: *d-camphornitronate*,  $l-[\text{Ir en}_3](d\text{-C}_{10}\text{H}_{15}\text{O}_8\text{N})_3$ ; *bromide*, ( $+ 2\text{H}_2\text{O}$ ),  $[\alpha]_C - 36^{\circ}$ ,  $[\alpha]_D - 50^{\circ}$ ,  $[\alpha]_E - 66.5^{\circ}$ ; *nitrate*,  $[\alpha]_C - 41.5^{\circ}$ ,  $[\alpha]_D - 57.5^{\circ}$ ,  $[\alpha]_E - 76^{\circ}$ ; *perchlorate*,  $[\alpha]_C - 34^{\circ}$ ,  $[\alpha]_D - 47.5^{\circ}$ ,  $[\alpha]_E - 63^{\circ}$ .  
T. H. P.

### Attempts to Prepare Derivatives of Diaminoacetylene.

PAUL RUGGLI (*Helv. Chim. Acta*, 1920, 3, 559—572. Compare A., 1917, i, 22).—With the object of obtaining derivatives of diaminoacetylene, those methods of decomposition which usually yield amines with one carbon atom less than the original compounds have been applied to acetylenedicarboxylic, dibromomaleic, and dibromofumaric acids. The only method giving promising results is that in which the hydrazide and azide form intermediate steps; with dibromomaleic acid hydrazine forms a closed ring hydrazide, with dibromofumaric acid degradation occurs in the desired direction, but has not as yet been carried sufficiently far. Unlike iminazole itself, tribromoiminazole yields no ethylene derivative, but merely a benzoyl compound when treated with benzoyl chloride.

Details are given for obtaining large quantities of bromine-free acetylenedicarboxylic acid by Bandrowski's method (this Journ., 1877, ii, 592; compare Michael, A., 1893, i, 144; von Baeyer, A., 1885, 759, 1198).

Treatment of dibromomaleic acid in pyridine solution with zinc dust yields, in the hot, resinified products, and in the cold only the *pyridine* salt of the acid,  $C_4H_2O_4Br_2 \cdot C_5NH_5$ , m. p.  $120^\circ$  (decomp.); no indications of the existence of a normal salt were obtained.

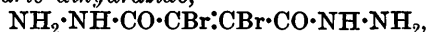
Ethyl acetylenedicarboxylate, prepared by esterification of the acid, forms crystals, m. p.  $1-2^\circ$ ,  $D_4^{25}$  (liquid) 1.0690. When prepared by reducing ethyl dibromomaleate with zinc dust, the ester is accompanied by a considerable proportion of resinous matter which cannot be distilled (compare Michael, *loc. cit.*).

The action of hydroxylamine on ethyl acetylenedicarboxylate in presence of sodium ethoxide yields the crystalline, hygroscopic sodium salt,  $NOH \cdot C(ONa) : C : C \cdot CO_2Na$ , or possibly

$CO_2Na \cdot C(NH \cdot OH) : CH \cdot CO_2Na \rightleftharpoons CO_2Na \cdot C(NO_2H) \cdot CH_2 \cdot CO_2Na$ , which forms an alkaline, aqueous solution, decolorises permanganate instantaneously, explodes slightly when heated, and with ferric chloride gives the deep violet coloration or precipitate characteristic for hydroxamic acids. Benzoylation by the Schotten-Baumann method gave small proportions of a crystalline compound, which was not examined further. When liberated by the action of dilute acid, the hydroxamic acid itself undergoes decomposition.

Chlorofumaric chloride,  $COCl \cdot CCl : CH \cdot COCl$  (compare Perkin, T., 1888, 53, 696; Ruggli and Hartmann, this vol., i, 636), prepared by the action of phosphorus pentachloride on acetylenedicarboxylic acid, has b. p.  $73-75^\circ/20$  mm.

*Dibromofumaric dihydrazide*,



prepared from dibromofumaric chloride and hydrazine hydrate, forms crystals decomposing at about  $154^\circ$ . In this preparation most of the material is converted into a brown powder, which carbonises at a high temperature.

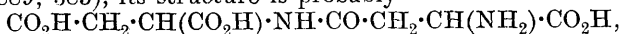
*Dibromofumaric diazide*,  $N_3 \cdot CO \cdot CBr : CBr \cdot CO \cdot N_3$ , obtained by treating the dihydrazide with nitrous acid, forms a white powder, and in the dry state explodes violently when gently rubbed. When heated with alcohol it yields nitrogen and a crystalline compound which is evidently diamidodibromoethylene carbamate, and is to be investigated.

2:4:5-Tribromo-1-benzoylglyoxaline,  $NBz \begin{matrix} \swarrow CBr : N \\ \searrow CBr : CBr \end{matrix}$ , forms stout crystals, m. p.  $101-102^\circ$ . T. H. P.

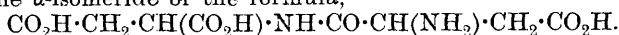
**Dipeptide of Aspartic Acid and Function of Asparagine in Plants.** C. RAVENNA and G. BOSINELLI (*Gazzetta*, 1920, 50, i, 281—288; *Atti R. Accad. Lincei*, 1920, [v], 29, i, 278—282).—When boiled, aqueous solutions of asparagine yield the dipeptide of aspartic acid, together with a little aspartic acid. Neither the latter nor its ammonium salts give the dipeptide under similar conditions (compare this vol., i, 150, 151, 373). The fundamental function of asparagine and of amides of amino-acids generally in plants appears to be to render possible the synthesis of polypeptides

and hence that of proteins; the results of the experiments with aspartic acid indicate that direct formation of proteins from the simple amino-acids does not occur.

Since the dipeptide obtained by the authors is formed only from asparagine, to which Piutti ascribes the structure of  $\beta$ -asparagine (A., 1889, 383), its structure is probably



whereas Fischer and Koenigs' dipeptide (A., 1907, i, 486) is probably the  $\alpha$ -isomeride of the formula,



T. H. P.

**Trichloroacetimino-methyl and -ethyl Ethers.** WILHELM STEINKOPF and RUDOLF SEMMIG (*Ber.*, 1920, **53**, [B], 1149—1152).—The conversion of nitriles into imino-ethers has been supposed by Houben (A., 1913, i, 958) to occur in accordance with the scheme

$\text{R}\cdot\text{C}\text{:}\text{N} + \text{HCl} \rightarrow \text{R}\cdot\text{CCl}\text{:}\text{NH} \xrightarrow{\text{MeOH}} \text{R}\cdot\text{C}(\text{OMe})\text{:}\text{NH} + \text{HCl}$ . Although generally agreeing with this view, the authors do not consider it applicable to the special case of trichloroacetone nitrile, which is converted by methyl alcohol in the absence of hydrogen chloride into trichloroacetiminomethyl ether and in the presence of the acid into trichloroacetamide (compare Steinkopf, A., 1907, i, 488). Further examination of the action shows that catalytic influences play a most important part, and, of these, the presence of trichloroacetamide in the nitrile and of acetone in the methyl alcohol appears to be the most important; with pure materials, the presence of hydrogen chloride greatly diminishes the rate of reaction. Similarly, pure ethyl alcohol does not react with nitrile containing amide, but action may be caused to occur both with pure and contaminated nitrile if a few drops of acetone are added. *Trichloroacetiminoethyl ether*,  $\text{CCl}_3\cdot\text{C}(\text{OEt})\text{:}\text{NH}$ , is a highly unstable substance, b. p.  $74\text{--}79^\circ/35\text{ mm.}$ , which could not be isolated in the pure state.

H. W.

**Mercuric Oxycyanide.** A. J. JONES (*Pharm. J.*, 1920, **105**, 87—89).—This compound may be prepared by grinding together 40 grams of mercuric cyanide, 30 grams of yellow mercuric oxide, and 15 c.c. of water for fifteen minutes; 0.5 c.c. of 20% sodium hydroxide is then added, and the stirring continued with the addition of further small quantities of water. After about eighteen hours the mass is diluted with 200 c.c. of water, rendered slightly acid with acetic acid, using phenolphthalein as indicator, and added to 700 c.c. of boiling water containing 20 grams of mercuric cyanide. The mixture is boiled until solution is almost complete, filtered, and cooled. The crystals are collected, washed with a small quantity of cold water, and dried over sulphuric acid. With more concentrated solutions than mentioned above, separated crystals of the oxycyanide are liable to decompose, and explosion has occurred during the preparation of the compound. W. P. S.

**The Preparation of Trimethylarsine and Trimethylarsine Selenide.** R. R. RENSHAW and G. E. HOLM (*J. Amer. Chem. Soc.*, 1920, **42**, 1468—1471).—For the preparation of trimethylarsine two methods were examined. In the first case arsenic trichloride or tribromide was allowed to act on magnesium methyl iodide in ethereal solution, the whole being cooled in ice. By this method apparently at least one other volatile compound, in addition to trimethylarsine, having a stronger and more penetrating odour, was produced. The second method was by the action of arsenic trichloride on zinc methyl in ethereal solution. Owing to the difficulty of separating the ether and the resulting trimethylarsine, it was found advisable to replace the ether by xylene, and then satisfactory yields of pure trimethylarsine, b. p. 51.9—52°/736 mm.,  $D_{25}^{22}$  1.124, were obtained.

When finely powdered selenium was added to the crude ethereal solution of trimethylarsine prepared by the first method, *trimethylarsine selenide*,  $\text{AsMe}_3\text{Se}$ , was obtained. It is very unstable in air, giving off an odour similar to that of trimethylarsine. W. G.

**Process for the Preparation of Arsine Derivatives.** ANDRÉ JOB and HENRI GUINOT (Brit. Pat. 144806).—The nitriles of the general formula  $\text{R}_2\text{AsCN}$ , where R is a fatty or aromatic group, are converted into amides and acids of the type  $\text{AsR}_2\cdot\text{CO}\cdot\text{NH}_2$  and  $\text{AsR}_2\cdot\text{CO}_2\text{H}$  by the general methods for the hydration of nitriles. For example, cacodyl cyanide is converted into dimethylarsinoformic acid by boiling it with about three times its weight of 50% sulphuric acid for twelve hours. The acid is isolated through its calcium or barium salt and crystallised from acetone and alcohol. Diphenylarsinoformic acid is similarly obtained from diphenylarsine cyanide, or the amide may be first prepared by treating the cyanide in alkaline solution with the theoretical quantity of hydrogen peroxide, and be converted into the acid by subsequent treatment with nitrous acid. Diphenylarsinoformic acid is much less soluble in water than the dimethyl compound. It reddens blue litmus, and forms salts, the majority of which are very soluble in water. G. F. M.

**The Preparation of Zinc Methyl.** R. R. RENSHAW and C. E. GREENLAW (*J. Amer. Chem. Soc.*, 1920, **42**, 1472—1474).—For the preparation of a suitable zinc-copper couple it is recommended to mix nine parts of zinc powder passing a 30-mesh sieve with one part of copper precipitated from solution by zinc, and heat the mixture gradually in a current of hydrogen in a combustion tube, the tube being rotated rapidly, until the zinc turns first a yellow colour and then forms into little pellets of a tarnished lead colour. The heating is then stopped, the couple cooled in hydrogen and used. Methyl acetate is used as a catalyst for the preparation of zinc methyl, 1 c.c. being added to 110 grams of methyl iodide before it is run on to the zinc-copper couple. The mixture is left overnight and then heated at 60° next day, con-

densation being complete in about seven hours. It is noted that at ordinary temperatures zinc methyl iodide dissociates to give enough zinc methyl to cause the vapour above to inflame spontaneously when exposed to the air.

W. G.

**The Energy Content of Polymethylene Rings.** WALTER HÜCKEL (*Ber.*, 1920, **53**, [B], 1277—1283).—The author has applied to polymethylene rings the considerations recently used by Fajans and von Steiger in calculating the heats of combustion of aliphatic and aromatic hydrocarbons (this vol., ii, 354, 355). The heat of combustion of the methylene group in each ring is obtained by dividing the heat of combustion of the necessary compound by the number of carbon atoms contained in it, and the difference between these values and 158 Cal. (the value for the  $\text{CH}_2$  group in a normal carbon chain) is a measure of the abnormal energy content of the rings. In this manner, the values 170, 168.5, 165.5, 159, and 158 are obtained for the methylene group in ethylene, *cyclopropane*, *cyclobutane*, *cyclopentane*, and *cyclohexane* respectively. These results are in good accord with Baeyer's strain theory. Using the formula developed by Fajans (*loc. cit.*), the energy of the C-C linking in the various rings is calculated to 126, 127.2, 130.1, 136.5, 137.5, 138.5, and 139 in ethylene, *cyclopropane*, *cyclobutane*, *cyclopentane*, *cyclohexane*, *cycloheptane*, and decahydronaphthalene respectively, the data being in agreement with Baeyer's strain theory as far as the lower members are concerned. The values obtained for methyl*cyclobutane*, methyl*cyclopentane*, and *cycloheptane*, however, require further explanation.

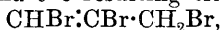
Much of the confusion which has existed with regard to the relative stability of different ring systems is due to inexact comparison. Thus, for example, it has been shown by Berthelot that the union of bromine with *cyclopropane* is accompanied by the development of 9.4 Cal. more than the union of bromine with propylene, and the conclusion is drawn that the *cyclopropane* ring is the more unstable. Actually, the processes are not completely similar, since different types of bond are broken; in the case of propylene, a double bond is opened (energy consumption, 126.5 Cal.), and the other passes into the normal linking (energy evolution,  $137.5 - 126.5 = 11$  Cal.), there being thus a total consumption of 115.5 Cal. With *cyclopropane*, the calculated values are: consumption, 127; evolution,  $2(137.5 - 127) = 21$ , or a total consumption of 106 Cal. The difference, therefore, is 9.5 Cal., which agrees excellently with Berthelot's experimental figure.

H. W.

**The Phenylpropinenes.** R. LESPIEAU and GARREAU (*Compt. rend.*, 1920, **171**, 111—113).—By the action of benzyl chloride on monosodium acetylide, the principal product is the phenylpropinene,  $\text{CPh:CMe}$ . If the method of Lespieau and Bourguel (this vol., i, 520) is used, *epidibromohydrin* gives with magnesium phenyl bromide  $\beta$ -*bromo- $\alpha$ -phenylpropylene*,  $\text{CH}_2\text{Ph}\cdot\text{CBr}\cdot\text{CH}_2$ , m. p.  $-12.5^\circ$ , b. p.  $102^\circ/17$  mm.,  $D_0^{20}$  1.39, which when treated



with alcoholic potassium hydroxide at  $110^{\circ}$  gives the propinene mentioned above. If  $\beta$ -bromo- $\alpha$ -phenylpropylene is brominated, it yields  $\beta\beta\gamma$ -tribromo- $\alpha$ -phenylpropane, b. p.  $175$ — $176^{\circ}/18$  mm., which when reduced with sodium in alcohol gives a compound, which with zinc in alcohol gives an acetylenic hydrocarbon, although the yields throughout are very small. If epidibromohydrin is brominated and the resulting tribromopropene,



is condensed with magnesium phenyl bromide in excess, a considerable yield of  $\gamma$ -phenyl- $\Delta^2$ -propinene,  $\text{CH}_2\text{Ph}:\text{C}:\text{CH}$ , b. p.  $70$ — $71^{\circ}/20$  mm., is obtained, which gives silver and copper derivatives. The cuprous derivative when treated with excess of iodine gives  $\beta\gamma\gamma$ -tri-iodo- $\alpha$ -phenylpropylene,  $\text{CH}_2\text{Ph}:\text{CI}:\text{CI}_2$ , m. p.  $84$ — $85^{\circ}$ . W. G.

**Examination of Nitro-compounds by means of Titanium Chloride and Sulphate.** C. F. VAN DUIN (*Rec. trav. chim.*, 1920, **39**, 578—585).—It is recommended to replace the titanium chloride by titanium sulphate in Knecht's method for determining the nitro-nitrogen in nitro-compounds in the case of feebly substituted compounds.

The author has successfully used titanous chloride for the partial reduction of *s*-trinitrobenzene, obtaining a 50% yield of dinitroaniline.

From a study of the reduction of 2:3:4:6-tetranitroaniline and of trinitromethylnitroaminophenol by titanous chloride, it is argued that the structure of the nitro-group in position 3 is given by  $\cdot\text{NO}_2$ , and not by  $\cdot\text{O}\cdot\text{NO}$ . W. G.

**The Action of the Grignard Reagent on Aromatic Nitro-compounds.** HARRY HEPPWORTH (*T.*, 1920, **117**, 1004—1012).

**Experiments on Halogenation. The Direct Displacement of Negative Groups by Halogen in the Aromatic Series. I. The Displacement of the Nitro-group by Bromine.** SURENDRA NATH DHAR (*T.*, 1920, **117**, 993—1001).

**The Replaceability of Halogens. I. Comparative Replaceability of Chlorine, Bromine, and Iodine in the Halogenonitrobenzenes.** HARTWIG FRANZEN and ERICH BOCKHACKER (*Ber.*, 1920, **53**, [B], 1174—1179).—The data recorded with regard to the relative ease of replacement of the halogens in aromatic compounds are somewhat conflicting, and, as the observations were usually made for preparative purposes, are insufficiently exact to allow any generalisations on the subject. A series of comparative experiments with the halogenonitrobenzenes has therefore been undertaken, the present observations dealing exclusively with alcoholic solutions. In general, the substance (5MM) is mixed with the base—piperidine, diethylamine, ammonia, sodium ethoxide—(25MM), and either preserved at  $0^{\circ}$  or at the ordinary tempera-

ture, or heated at the boiling point of the solution or at 100°. The course of the reaction is followed by pouring the solution, after definite intervals of time, into water, adding nitric acid in excess, filtering from precipitated organic matter, and estimating the halogen acid as silver haloid. The results that have been obtained may be summarised as follows. In the cases of the action of diethylamine, piperidine, and sodium ethoxide on the 1-halogeno-2-nitrobenzenes and 1-halogeno-4-nitrobenzenes, iodine is least easily replaced. With diethylamine and piperidine, bromine is more readily replaced than chlorine, but whilst with sodium ethoxide this is also true in the case of *o*-chloronitrobenzene, the reverse holds with *p*-chloronitrobenzene. Reaction of 1-halogeno-2:4-dinitrobenzenes with ammonia, piperidine, aniline, and sodium ethoxide occurs least readily with the iodo-compounds; with ammonia and sodium ethoxide, chlorine is replaced more rapidly than bromine, whilst with piperidine and aniline, bromine reacts more readily than chlorine. There is no general parallelism between the strength of the base and its power of effecting replacement of halogens in the halogenonitrobenzenes in the sense that the stronger base reacts more rapidly than the weaker; the reverse can also be the case.

H. W.

### Some New Derivatives of Mesitylene and $\psi$ -Cumene.

CHARLES STANLEY GIBSON (T., 1920, 117, 948—957).

### Some Nitro-derivatives of Naphthalene and Anthraquinone.

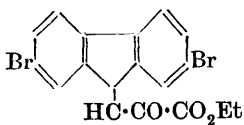
SURENDRA NATH DHAR (T., 1920, 117, 1001—1004).

**The Fluorene Series. II.** ADOLF SIEGLITZ (*Ber.*, 1920, 53, [B], 1232—1241. Compare this vol., i, 27).—The condensation of fluorene with aromatic aldehydes has been further investigated. It is found that 2:7-dibromofluorene reacts with unexpected ease with aromatic aldehydes, yielding products which are solid and characterised by marked ability to crystallise, so that they are very suitable for the identification of the aldehydes. Unfortunately, it does not appear possible to extend the reaction to aliphatic aldehydes or ketones. The colour of the substituted fulvenes is uniformly deeper than that of the substances derived from fluorene itself, but the halochromic colorations with sulphuric acid in the new series are not characteristic. The following individual compounds are described: 9:9'-*isophthalylidenedifluorene*, pale yellow leaflets, m. p. 178—179°; 9-*p*-*bromobenzylidenefluorene*, yellow needles, m. p. 144°; 9-*m*-*iodobenzylidenefluorene*, yellow, microscopic needles, m. p. 103°; 9-*p*-*iodobenzylidenefluorene*, pale yellow, flat prisms, m. p. 121°; 9-*pi-peronylidenefluorene*, yellow needles, m. p. 72—73° [*picrate*, dark red needles with green reflex, m. p. 194—195° (decomp.)]; 9-*anisylidenefluorene picrate*, red needles, m. p. 121° (decomp.); 9-*furylidenefluorene picrate*, dark red needles, m. p. 146—147° (decomp.).

2:7-Dibromofluorene, m. p. 164°, is conveniently prepared by the gradual addition of bromine to an ice-cold solution of fluorene

in chloroform. The condensation products are prepared by adding the calculated amount of the aldehyde dissolved in alcohol (20 c.c.) to a boiling solution of sodium (0.5 gram) and dibromofluorene (1.5 grams) in absolute alcohol (100 c.c.); the solution is rapidly heated to boiling, and subsequently preserved for a day, after which the product is separated; a red substance, probably 2:2':7:7'-tetrabromo- $\alpha\delta$ -dibiphenylene- $\Delta^{\gamma}$ -butadiene, is formed as by-product. The following products are described: 2:7-dibromo-9-benzylidenefluorene, long, pale yellow rods, m. p. 98—99°; 2:7-dibromo-9-o-methylbenzylidenefluorene, orange-yellow leaflets, m. p. 141—142°; 2:7-dibromo-9-m-methylbenzylidenefluorene, yellow prisms, m. p. 95—96°; 2:7-dibromo-9-p-methylbenzylidenefluorene, yellow, matted needles, m. p. 140—141°; 2:7-dibromo-9-o-ethylbenzylidenefluorene, yellow prisms and leaflets, m. p. 132—133°; 2:7-dibromo-9-m-ethylbenzylidenefluorene, yellow rods, m. p. 82—83°; 2:7-dibromo-9-p-isopropylbenzylidenefluorene, yellow needles, m. p. 116—117°; 2:2':7:7'-tetrabromo-9:9'-isophthalylidenedifluorene, slender, pale yellow needles, which do not melt below 280°; 2:7-dibromo-9-p-aldehydbenzylidenefluorene, orange-yellow needles, m. p. 218—219°; 2:2':7:7'-tetrabromoterephthalylidenedi-9:9'-fluorene, dark orange leaflets, which do not melt below 300°; 2:7-dibromo-9-o-chlorobenzylidenefluorene, canary-yellow needles and rods, m. p. 168—169°; 2:7-dibromo-9-m-chlorobenzylidenefluorene, pale yellow, microcrystalline needles, m. p. 136—137°; 2:7-dibromo-9-p-chlorobenzylidenefluorene, long, yellow, matted needles, m. p. 211—212°; 2:7-dibromo-9-m-bromobenzylidenefluorene, small, yellow needles, m. p. 152—153°; 2:7-dibromo-9-p-iodobenzylidenefluorene, orange-yellow needles, m. p. 207—208°; 2:7-dibromo-9-o-methoxybenzylidenefluorene, orange-yellow leaflets, m. p. 154—155°; 2:7-dibromo-9-p-methoxybenzylidenefluorene, deep yellow needles, m. p. 132—133°; 2:7-dibromo-9-piperonylidenefluorene, yellow needles, m. p. 159—160°; 2:7-dibromo-9-o-nitrobenzylidenefluorene, orange-yellow needles, m. p. 201—202°; 2:7-dibromo-9-m-nitrobenzylidenefluorene, small, yellow crystals, m. p. 154—155°; 2:7-dibromo-9-p-nitrobenzylidenefluorene, orange-yellow, microcrystalline powder, m. p. 195—196°; 2:7-dibromo-9-2'-chloro-5'-nitrobenzylidenefluorene, yellow needles, m. p. 212—213° after softening at 190° (m. p. 216—218° after resolidification); 2:7-dibromo-9-cinnamylidenefluorene, slender, deep yellow needles, m. p. 206—207°; 2:7-dibromo-9-furylidenefluorene, long, greenish-yellow needles, m. p. 190—191°.

Ethyl oxalate condenses with 2:7-dibromofluorene in the presence of sodium ethoxide to form ethyl 2:7-dibromofluoreneoxalate (annexed formula), shining, yellow needles, m. p. 176°; the substance gives a brown coloration with ferric chloride, and yields a benzoyl derivative, canary-yellow rods, m. p. 152—153°.



H. W.

**cycloHexylamines. II.** A. SKITA and H. ROLFES (*Ber.*, 1920, 53, [B], 1242—1255. Compare Skita and Berendt, this vol., i, 27).—In connexion with Skita's process for the reduction of aromatic amines to cyclohexylamines, the general behaviour of the latter class of substances has been more fully investigated.

[With KARL HILS and GUSTAV KIRCHHOFF.]—*Ammonium dicyclohexyl dithiocarbamate*,  $C_6H_{11} \cdot NH \cdot CS \cdot S \cdot NH_3 \cdot C_6H_{11}$ , m. p.  $160^\circ$ , is readily prepared by the direct union of cyclohexylamine and carbon disulphide; it is converted by distillation with an aqueous solution of mercuric chloride into cyclohexylthiocarbimide, b. p.  $219^\circ/746$  mm., which may also be obtained by the distillation of dicyclohexylthiocarbamate, cubes, m. p.  $180$ — $181^\circ$ , with glacial phosphoric acid. cycloHexylthiocarbimide combines with ammonia to yield cyclohexylthiocarbamide,  $NH_2 \cdot CS \cdot NH \cdot C_6H_{11}$ , m. p.  $161$ — $162^\circ$ , with aniline to give phenylcyclohexylthiocarbamide, m. p.  $150$ — $151^\circ$ , and with absolute alcohol at  $100^\circ$  to form cyclohexylthiourethane, m. p.  $45$ — $46^\circ$ .

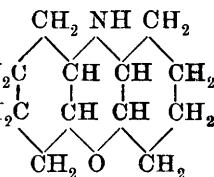
Dicyclohexylcarbamide, m. p.  $229$ — $230^\circ$ , is obtained from cyclohexylamine and carbonyl chloride, and is converted by phosphoric oxide into cyclohexylcarbimide,  $C_6H_{11} \cdot N : C : O$ , b. p.  $175^\circ/750$  mm.; the latter is transformed by ammonia, aniline, and ethyl alcohol into cyclohexylcarbamide, m. p.  $184^\circ$ , phenylcyclohexylcarbamide, colourless needles, m. p.  $182^\circ$ , and cyclohexylurethane, m. p.  $57^\circ$ .

cycloHexylamine is converted by methyl sulphate in warm ethereal solution into cyclohexylamine methyl sulphate, m. p.  $103^\circ$ , and a basic portion, which, after purification through the acetyl derivative, b. p.  $249^\circ/740$  mm., or the benzoyl derivative, needles, m. p.  $76^\circ$ , yields *N*-methylcyclohexylamine, b. p.  $147^\circ$ , identical in all respects with the product obtained previously (*loc. cit.*) by the catalytic hydrogenation of methylaniline. It was further identified by conversion into the picrate, m. p.  $170^\circ$ , and into nitroso-*N*-methylcyclohexylamine, yellow liquid, b. p.  $121^\circ/12$  mm. (*hydrochloride*, needles, m. p.  $176^\circ$ ). *N*-Dimethylcyclohexylamine, b. p.  $165^\circ$ , is prepared in 80% yield by the action of formic acid and formaldehyde on cyclohexylamine at  $120^\circ$ ; the picrate has m. p.  $181^\circ$ . The base is converted by methyl iodide into trimethylcyclohexylammonium iodide, needles, m. p.  $277^\circ$ , which is transformed by silver oxide into the corresponding hydroxide, which decomposes into tetrahydrobenzene, trimethylamine, and water when its aqueous solution is evaporated. When treated with nitrosyl chloride in cold ethereal solution, *N*-dimethylcyclohexylamine undergoes a remarkable change, whereby *N*-nitroso-*N*-methylcyclohexylamine is produced; the latter is reduced by tin and hydrochloric acid to *N*-methylcyclohexylamine. A similar instance is presented by *N*-methyldicyclohexylamine,  $C_6H_{11} \cdot NMe \cdot C_6H_{11}$ , which with nitrosyl chloride gives nitrosodicyclohexylamine,  $C_6H_{11} \cdot N(NO) \cdot C_6H_{11}$ , m. p.  $105^\circ$ , which is reduced to dicyclohexylamine by zinc and hydrochloric acid.

Ethyl iodide reacts readily with cyclohexylamine, giving *N*-ethylcyclohexylamine, identical with the product obtained by the cata-

lytic reduction of ethylaniline (*loc. cit.*); the *benzoyl* and *acetyl* derivatives have b. p.'s  $201^{\circ}$  and  $256^{\circ}/740$  mm. respectively, whilst the *picrate*, yellow crystals, and *hydrochloride*, have m. p.'s  $133^{\circ}$  and  $184^{\circ}$  respectively. *Nitroso-N-ethylcyclohexylamine* is an oil, b. p.  $130^{\circ}/12$  mm. When treated with ethyl iodide and potassium hydroxide, *cyclohexylamine* is transformed into *N-diethylcyclohexylamine*, b. p.  $193^{\circ}$ .

Acetanilide is but little attacked by hydrogen under conditions similar to those adopted for the reduction of aniline to *cyclohexylamine*; by increasing the concentration of the catalyst and raising the temperature to  $70-80^{\circ}$ , it can be completely hydrogenated to *acetylcyclohexylamine*, m. p.  $107^{\circ}$ . Under similar conditions, the isomeric acetotoluidides can be completely converted into their hexahydro-derivatives; *acetyl-2-methylcyclohexylamine* has b. p.  $154^{\circ}/20$  mm., m. p.  $50^{\circ}$ , the corresponding 3-derivative has b. p.  $152^{\circ}/18$  mm., m. p.  $74-75^{\circ}$ , whilst the 4-compound has b. p.  $152^{\circ}/12$  mm., m. p.  $77-78^{\circ}$ . *p*-Ethoxyacetanilide is hydrogenated with remarkable ease, but the product is *acetylcyclohexylamine*, m. p.  $106-107^{\circ}$ . The elimination of the ethoxy-group is the more note worthy since anisole and phenetole are reduced to *cyclohexyl methyl ether*, b. p.  $140^{\circ}/740$  mm., and *cyclohexyl ethyl ether*, b. p.  $144-145^{\circ}/738$  mm., under precisely similar conditions. Anisidine and phenetidine are, however, converted into a mixture of *dicyclohexylamine* and *cyclohexylamine* (small quantities of the latter are very rapidly and conveniently identified by conversion into *p-toluenesulphoncyclohexylamide*,  $C_6H_4Me \cdot SO_2 \cdot NH \cdot C_6H_{11}$ , m. p.  $86^{\circ}$ ). A similar mixture of bases is obtained from *p*- and *m*-aminophenol; *o*-aminophenol gives a mixture of *cyclohexylamine* and *dodecahydrophenoxazine* (annexed formula), m. p.  $103-104^{\circ}$  (*benzoyl* derivative, pyramids, m. p.  $160-161^{\circ}$ ).  
H. W.



### Crystalline Form of 2:4-Dichloro-3-nitroacetanilide.

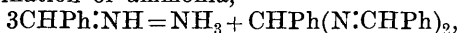
MARIA DE ANGELIS (*Atti R. Accad. Lincei*, 1920, [v], 29, i, 247-251).—This compound is dimorphous; both the  $\alpha$ - and  $\beta$ -modifications form crystals belonging to the prismatic class of the monoclinic system; for the former,  $a:b:c=1.1507:1:1.1348$ ,  $\beta=66^{\circ}23'$ , and for the latter,  $a:b:c=1.5792:1:1.0952$ ,  $\beta=62^{\circ}23.5'$ .

T. H. P.

**Catalysts which Promote Reaction between Aniline and Ethyl Alcohol.** T. B. JOHNSON, A. J. HILL, and J. J. DONLEAVY (*J. Ind. Eng. Chem.*, 1920, 12, 636-644).—No alkylation results when aniline is heated with ethyl alcohol in an autoclave in the presence of calcium oxide. Aniline hydrochloride heated with ethyl alcohol for eight hours in an autoclave at  $175-180^{\circ}$ , in the presence of sodium bromide, cupric chloride, and calcium chloride, gives good yields of diethylaniline containing only about 5% of mono-

ethylaniline. Substitution of aniline for an equivalent quantity of aniline hydrochloride yields a product largely composed of monoethylaniline. Zinc chloride probably has a dealkylising action as well as a dehydrating effect, and is less effective as a catalyst than calcium chloride, whilst potassium iodide is slightly more effective than sodium bromide. The use of 95% alcohol instead of absolute ethyl alcohol causes the yield of diethylaniline to be lowered by about 7%. The addition of the sodium bromide has the effect of lowering the amount of monoethylaniline by about 2%, whilst pyridine has a negative catalytic action, and raises it by about 11% (compare *J. Soc. Chem. Ind.*, 1920, September). C. A. M.

**Catalytic Hydrogenation of Nitriles; Mechanism of the Formation of Secondary and Tertiary Amines.** GEORGES MIGNONAC (*Compt. rend.*, 1920, **171**, 114—117).—When benzonitrile is hydrogenated in absolute alcohol in the presence of nickel as catalyst at the ordinary temperature (compare this vol., i, 442), the operation being interrupted when one molecule of hydrogen has been fixed, the product consists of one part of benzylamine and 2—2·5 parts of benzylidenebenzylamine,  $\text{CHPh:N}\cdot\text{CH}_2\text{Ph}$ , the latter, if the hydrogenation is continued, being converted into dibenzylamine. The course of the reaction is considered to be that benzaldimine is first formed, and that this then rapidly condenses with the elimination of ammonia,



and that the condensation product then undergoes hydrogenation, giving benzylamine and benzylidenebenzylamine.

Under similar conditions, *o*-toluonitrile gives *o*-methylbenzylamine and *o*-methylbenzylidene-*o*-methylbenzylamine, b. p. 170—171°/5 mm., and *p*-toluonitrile gives *p*-methylbenzylamine and *p*-methylbenzylidene-*p*-methylbenzylamine, m. p. 83—84°, b. p. 160°/3·5 mm.

W. G.

**Hydrogenation in the Naphthalene Series.** F. M. ROWE (*J. Soc. Chem. Ind.*, 1920, **39**, 241—246).— $\alpha$ -Naphthylamine is reduced by sodium and amyl alcohol to *ar*-tetrahydro- $\alpha$ -naphthylamine, but, in the presence of ethyl or butyl alcohol, only dihydroderivatives are formed. Preliminary experiments indicate that this difference cannot be ascribed solely to differences in temperature of the experiment. A similar result is observed when reduction is effected in the presence of an indifferent solvent, such as toluene or solvent naphtha (compare D.R.-P. 305347, 306724). A more extended study shows that  $\alpha$ -naphthylamine is reduced by sodium and an alcohol to 5:8-dihydro-1-naphthylamine; the latter, under suitable conditions of temperature and alkali alkoxide concentration, undergoes isomerisation to 7:8-dihydro-1-naphthylamine, which, unlike the 5:8-isomeride, is further reduced to *ar*-tetrahydro- $\alpha$ -naphthylamine. The failure to obtain the tetrahydro-compound when amyl alcohol was not used is probably to be explained by the absence of conditions suitable for the isomerisa-

tion. Reduction of naphthalene takes place similarly to that of  $\alpha$ -naphthylamine; 1:4-dihydronaphthalene is initially formed, which, under suitable conditions, is isomerised to 1:2-dihydronaphthalene and then reduced to tetrahydronaphthalene.

The direct hydrogenation of naphthalene and  $\alpha$ -naphthylamine has also been studied, the experiments being performed by bubbling hydrogen at the ordinary pressure through the purified substance, either molten or dissolved in a suitable solvent, in presence of nickel deposited on kieselguhr, in a glass vessel fitted with a condenser and an agitator capable of being driven at a high speed. Temperatures varying from  $100^{\circ}$  to the respective boiling points of naphthalene and  $\alpha$ -naphthylamine were used with these substances in the absence of a solvent without result, except that there was an appreciable evolution of ammonia in the latter case, particularly at the higher temperatures. Negative results were also obtained with  $\alpha$ -naphthylamine dissolved in boiling light petroleum, toluene, or solvent naphtha. The base, however, was reduced in boiling ethyl-alcoholic solution or, preferably, in boiling mixtures of ethyl alcohol with toluene or solvent naphtha; in the latter circumstances, 5:8-dihydro- $\alpha$ -naphthylamine was quantitatively formed, but the further reduction to tetrahydro- $\alpha$ -naphthylamine was not satisfactorily accomplished. Similarly, naphthalene could be hydrogenated in boiling ethyl-alcoholic solution, a mixture of products being invariably obtained, the main constituent of which is 1:4-dihydronaphthalene; prolongation of the action or treatment of 1:4-dihydronaphthalene in boiling ethyl-alcoholic solution led to the formation of some tetrahydronaphthalene, together with a mixture of liquids of lower boiling point which was not examined more closely, but probably consisted of more completely saturated derivatives.

H. W.

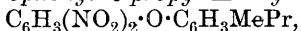
**Spontaneous Decomposition of  $\alpha$ -Aminophenyl- $\alpha$ -naphthylmethane.** II. S. BERLINGOZZI (*Gazzetta*, 1920, 50, i, 321—325. Compare this vol., i, 480).— $\alpha$ -Aminophenyl- $\alpha$ -naphthylmethane undergoes spontaneous decomposition at the ordinary temperature, with liberation of ammonia and formation of *di*-(naphthylbenzyl)-amine,  $\text{NH}(\cdot\text{CHPh}\cdot\text{C}_{10}\text{H}_7)_2$ , which forms minute, shining, white crystals, m. p.  $181^{\circ}$ . It is shown that the product, m. p.  $121^{\circ}$ , described by Busche and Leeffhelm (A., 1908, i, 152) as  $\alpha$ -aminophenyl- $\alpha$ -naphthylmethane, consists of a mixture of the latter with di-(naphthylbenzyl)-amine.

T. H. P.

**Oxynitration of Benzene [Formation of Nitrophenols].** LÉO VIGNON (*Bull. Soc. chim.*, 1920, [iv], 27, 547—550).—To obtain the best yield of nitrophenols in the action of nitric acid and mercuric nitrate on benzene it is advisable to use an excess of benzene, and the following proportions are recommended: 1000 grams of nitric acid (D 1.29—1.325), 25 grams of mercuric nitrate, and 500 grams of benzene, the mixture being heated on a water-bath for five to seven hours.

W. G.

**Derivatives of Diphenyl Ether.** ALFRED N. COOK, WM. C. EVANS, and DANIEL SHERK (*Proc. S. Dak. Acad. Sci.*, 1917, 2, 21—25).—2:4-Dinitrophenyl 6-propyl-m-tolyl ether,



sulphur-yellow needles, m. p.  $64^\circ$ , obtained by heating equal molecular quantities of potassium thymolate and 1-bromo-2:4-dinitrobenzene, yields on sulphonation a monosulphonic acid, pearly crystals (lead salt; barium salt with  $5.5\text{H}_2\text{O}$ ). 2-Nitrophenyl 5-propyl-o-tolyl ether, brownish-red liquid, b. p.  $222^\circ/20\text{ mm.}$ , forms a sulphonic acid, crystals with  $2\text{H}_2\text{O}$ , m. p.  $223\text{—}227^\circ$  (decomp.), of which the barium, calcium, and lead salts crystallise with 3, 6, and  $8\text{H}_2\text{O}$  respectively. CHEMICAL ABSTRACTS.

**Derivatives of the Sulphone of o-Cresol (o-Hydroxytolylsulphone).** FRÉDÉRIC REVERDIN and ANDRÉ ROETHLISBERGER (*Helv. Chim. Acta*, 1920, 3, 486—492).—The authors have prepared o-hydroxytolylsulphone by Zehenter's method (A., 1912, i, 444), and have studied certain of its derivatives.

The acetyl compound agrees in properties with Tassinari's product (A., 1889, 245). The benzoyl derivative,  $\text{SO}_2(\text{C}_6\text{H}_3\text{Me} \cdot \text{OBz})_2$ , prepared by either Schotten and Baumann's or Reverdin's method (A., 1918, i, 536), forms colourless, prismatic crystals, m. p.  $183\text{—}184^\circ$ . The dinitro-derivative, m. p.  $243^\circ$  (compare Zehenter, *loc. cit.*), yields an acetyl compound,  $\text{SO}_2(\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me} \cdot \text{OAc})_2$ , which forms deep yellow crystals, m. p.  $204\text{—}205^\circ$ , and a benzoyl compound,  $\text{SO}_2(\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me} \cdot \text{OBz})_2$ , m. p.  $179\text{—}180^\circ$ .

When treated with sulphuric acid (20%  $\text{SO}_3$ ), the dinitro-derivative is converted into an isomeride,  $\text{C}_{14}\text{H}_{12}\text{O}_8\text{N}_2\text{S}$ , which forms yellow crystals, m. p.  $209\text{—}210^\circ$ , and yields an acetyl derivative, crystallising in pale yellow plates, m. p.  $200\text{—}201^\circ$ .

Nitration of the acetyl derivative of the sulphone yields partly the acetyl dinitro-compound, melting at  $243^\circ$ , but is incomplete, and, if carried further, is accompanied by partial scission of the molecule. Nitration of the benzoyl derivative yields mainly a m-nitrobenzoyl-o-cresolsulphone, the nitro-group being introduced into the benzoyl residue.

Reduction of the dinitro-derivative, m. p.  $243^\circ$ , by means of tin and hydrochloric acid gives a double chloride of tin and the aminosulphone; the free aminosulphone forms pale brown needles, m. p.  $212^\circ$  (decomp.), is readily oxidised, gives solutions which colour in the air and yield a deep brown coloration with ferric chloride solution, and furnishes a highly stable diazo-derivative, crystallising in yellow needles. The compound obtained on reduction of the isomeric dinitro-compound, m. p.  $209\text{—}210^\circ$ , is not oxidised in solution by atmospheric oxygen, and yields a less stable diazo-derivative.

T. H. P.

**Derivatives of Trihalogen Tertiary Butyl Alcohol. III. The Benzoic Acid Ester of Trichloro-tert.-butyl Alcohol or Chloretone Benzoic Ester.** T. B. ALDRICH (*J. Amer. Chem. Soc.*, 1920, 42, 1502—1507. Compare A., 1916, i, 115; 1917, i, 77; 1919, i, 62).—A repetition of the work of Willgerodt and Dürr



(compare *J. pr. Chem.*, 1889, [ii], **39**, 286). It is now found that when molecular proportions of benzoyl chloride and chloretone (trichloro-*tert.*-butyl alcohol) are heated together on a water-bath until hydrogen chloride ceases to be given off, trichloro-*tert.*-butyl benzoate is obtained, and may be isolated in a crystalline form, m. p. 34—35°. It may be distilled under reduced pressure without appreciable decomposition, and is not readily hydrolysed, being much more stable than other esters of this alcohol. Pharmacological tests indicate that it possesses less hypnotic or anæsthetic properties, and is less toxic than the esters studied thus far (*loc. cit.*).

W. G.

**Amino-alcohols. Action of Amines on the Mono-esters (Acetates and Benzoates) of Chlorohydrins.** E. FOURNEAU and (MME) P. RAMART-LUCAS (*Bull. Soc. chim.*, 1920, [iv], **27**, 550—557).—Sodium benzoate acts on  $\alpha$ -chloropentan- $\gamma$ -ol in the presence of potassium iodide to give  $\alpha$ -benzoyloxy-pentan- $\gamma$ -ol, b. p. 171°/11 mm., 181°/20 mm., which with thionyl chloride in pyridine solution yields  $\gamma$ -benzoyloxy-pentan- $\alpha$ -ol, b. p. 165—167°/17 mm., 157—159°/12 mm. This chloro-ester when warmed with dimethylamine in benzene solution gives  $\alpha$ -dimethylamino- $\gamma$ -benzoyloxy-pentane, b. p. 170°/16 mm., which may also be obtained by the action of benzoyl chloride on  $\alpha$ -dimethylaminopentan- $\gamma$ -ol. When  $\alpha$ -chloropentan- $\gamma$ -ol is heated for four hours at 160—170° with potassium acetate it yields  $\gamma$ -acetoxy-pentan- $\alpha$ -ol, b. p. 113—114°/12 mm., which, with thionyl chloride, gives  $\alpha$ -chloro- $\gamma$ -acetoxy-pentane, b. p. 84—86°/14 mm. This chloroacetate with dimethylamine gives a mixture of bases, from which  $\alpha$ -dimethylamino- $\gamma$ -acetoxy-pentane can be isolated.  $\gamma$ -Chloro- $\alpha$ -phenylpropan- $\beta$ -ol with sodium benzoate gives a mixture of two benzoates, from which the chloro-compound can be prepared, and this with dimethylamine gives two bases, namely,  $\gamma$ -dimethylamino- $\alpha$ -phenylpropan- $\beta$ -ol, b. p. 153°/40 mm., and its benzoate, b. p. 220°/20 mm.

$\gamma$ -Chloro- $\alpha$ -phenylpropan- $\alpha$ -ol gives with sodium benzoate a benzoate, b. p. 230°/12 mm., which when treated with thionyl chloride, and then with dimethylamine, yields  $\gamma$ -dimethylamino- $\gamma$ -phenylpropyl benzoate, b. p. 230°/15 mm., giving a hydrochloride, m. p. 146°.

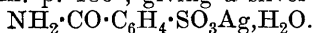
W. G.

**The Preparation of *o*-Nitrobenzoic Acid.** MARIE REIMER and ELIZABETH STEWART GATEWOOD (*J. Amer. Chem. Soc.*, 1920, **42**, 1475—1478).—The mixed *o*- and *p*-nitrotoluenes obtained from the nitration of toluene were oxidised by alkaline permanganate in concentrated solution (compare Bigelow, this vol., i, 20). The *o*- and *p*-nitrobenzoic acids were isolated by conversion into their methyl esters, which were then separated by fractional distillation under reduced pressure.

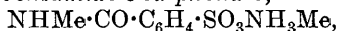
W. G.

***o*-Sulphobenzoic Anhydride and Benzamide- and Methylbenzamide-*o*-sulphonic Acids.** H. J. TAVERNE (*Rec. trav. chim.*, 1920, **39**, 542—548).—*o*-Sulphobenzoic anhydride was prepared by

the interaction of potassium hydrogen sulphobenzoate and phosphorus pentachloride, and by the action of acetyl chloride on the free acid. The anhydride prepared by either method had m. p. 130°, and molecular-weight determinations showed it to be an internal anhydride. By the action of dry ammonia on its benzene solution, it gave ammonium benzamide-*o*-sulphonate, from which the corresponding *barium* salt,  $(\text{NH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3)_2\text{Ba}, 6\text{H}_2\text{O}$ , was obtained, and this, on decomposition with dilute sulphuric acid, gave the free acid, m. p. 186°, giving a silver salt,



When a benzene solution of *o*-sulphobenzoic anhydride is saturated with methylamine, a crystalline precipitate of *methylammonium methylbenzamide-*o*-sulphonate*,



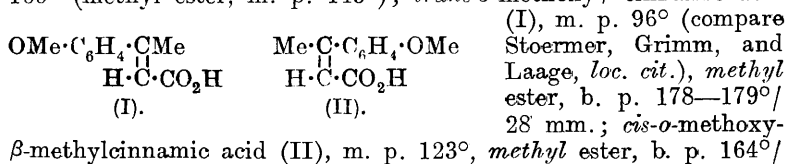
m. p. 189—190°, is obtained. This gives the corresponding *barium* salt,  $(\text{C}_8\text{H}_8\text{O}_4\text{NS})_2\text{Ba}, 4\text{H}_2\text{O}$ , which, on decomposition with sulphuric acid, gives *methylbenzamide-*o*-sulphonic acid*, m. p. 167—169°.

W. G.

**Catalytic Hydration of Nitriles.** A. MAILHE (*Compt. rend.*, 1920, **171**, 245—247).—Nitriles may be converted into the corresponding acids by passing their vapours, along with water vapour, over thorium oxide at a temperature of 420°.

W. G.

**Boiling Points of Esters of Stereoisomeric Cinnamic Acids.** R. STOERMER and KARL SANDOW (*Ber.*, 1920, **53**, [B], 1283—1289).—It was observed by Stoermer, Grimm, and Laage (A., 1917, i, 647) that the esters of *cis*-cinnamic acids uniformly boil about 12—15° lower than the esters of the corresponding stereoisomeric *trans*-acids, and that, as far as the evidence was available, this relationship held good even in those cases in which the *cis*-acid had a higher melting point than the *trans*-acid. The number of such instances was, however, somewhat restricted; in order, therefore, to secure further evidence on this point, the authors have prepared a further series of such pairs of acids, and have found their previous observation completely confirmed. The boiling points of the esters of stereoisomeric cinnamic acids appear to be a valuable criterion of the adherence of the free acid to the *allo*-series or otherwise. The alkyloxy- $\beta$ -methylcinnamic acids are obtained from 4-methylcoumarin by fission and subsequent alkylation, or by transformation of the *cis*-forms primarily obtained into the corresponding *trans*-forms by concentrated potassium hydroxide solution. Esterification of the acids is conveniently effected with methyl or ethyl sulphate in alkaline solution. The following substances are described: *trans-*o*-hydroxy- $\beta$ -methylcinnamic acid*, m. p. 160° (methyl ester, m. p. 143°); *trans-*o*-methoxy- $\beta$ -cinnamic acid*



28 mm., m. p. 44°; *trans*- $\alpha$ -ethoxy- $\beta$ -methylcinnamic acid, m. p. 111—112°, *methyl ester*, b. p. 160—161°/13 mm., m. p. 43°, *ethyl ester*, m. p. 53°, *amide*, m. p. 97°; *cis*- $\alpha$ -ethoxy- $\beta$ -methylcinnamic acid, m. p. 138°, *methyl ester*, b. p. 148—148·5°/13 mm., *ethyl ester*, b. p. 152°/11 mm., *amide*, m. p. 118°; *trans*- $\alpha$ -*n*-propoxy- $\beta$ -methylcinnamic acid, slender needles, m. p. 72°, *methyl ester*, b. p. 177°/20 mm.; *cis*- $\alpha$ -*n*-propoxy- $\beta$ -methylcinnamic acid, m. p. 108°, *methyl ester*, b. p. 167°/20 mm.; *trans*- $\alpha$ -*n*-butoxy- $\beta$ -methylcinnamic acid, colourless needles, m. p. 57°, *methyl ester*, b. p. 187—188°/24 mm.; *cis*- $\alpha$ -*n*-butoxy- $\beta$ -methylcinnamic acid, m. p. 74°, *methyl ester*, b. p. 175°/24 mm. H. W.

### Boiling Points of Esters of Stereoisomeric Unsaturated

**Acids.** R. STOERMER and H. KIRCHNER (*Ber.*, 1920, 53, [B], 1289—1299).—In previous communications (Stoermer, Grimm, and Laage, A., 1917, i, 647, Stoermer and Sandow, preceding abstract) it has been shown that the esters of the *cis*-form of stereoisomeric unsaturated cinnamic acids have a lower boiling point than the corresponding *trans*-compounds. The observations are now extended to the halogenated cinnamic acids, and the same regularity is observed in all cases in which the configuration of the acids can be regarded as definitely elucidated. In all, therefore, nineteen pairs of stereoisomeric esters have been investigated without leading to the discovery of an exception to the rule. Up to the present, however, only aromatic compounds have been considered; an attempt is therefore made to extend the observations to aliphatic compounds, and fumaric and maleic esters are chosen by reason of the close analogy in chemical behaviour of the phenyl and

H·C·CO

|| >

H·C·C(OMe)<sub>2</sub>

carboxyl groups. In this case, however, an exception appears to be presented which leads the authors to consider that methyl maleate may possibly have the annexed constitution; a certain amount of evidence in favour of this view is derived from spectrochemical observations and from analogy to the corresponding chlorides. The melting point of the free acids appears to be a very uncertain criterion of their adherence to the *cis*- or *trans*-series; still less reliance can be placed on the melting points of their esters or amides in this respect. It is interesting to note that the position of the halogen atom in the  $\alpha$ - and  $\beta$ -halogenated acids is practically without influence on the boiling points of the esters. The following compounds are described: *trans*- $\alpha$ -chlorocinnamic acid, m. p. 33—34°, *methyl ester*, b. p. 167° (corr.)/28 mm., 108—109°/0·5 mm.; *methyl cis*- $\alpha$ -chlorocinnamate, b. p. 153—154°/28 mm., 98—99°/0·6 mm.; *methyl trans*- $\alpha$ -bromocinnamate, m. p. 23°, b. p. 177—178° (corr.)/23 mm., 120—121°/0·6 mm.; *methyl cis*- $\alpha$ -bromocinnamate, b. p. 167·5—168·5° (corr.)/26 mm., 111°/0·6 mm.; *trans*- $\alpha$ -chlorocinnamamide, m. p. 121°, b. p. 216—217°/12 mm. (with partial sublimation), 158—160°/0·6 mm.; *cis*- $\alpha$ -chlorocinnamamide, m. p. 134°, b. p. 210°/13 mm., 153—154°/0·6 mm.; *trans*- $\alpha$ -bromocinnamamide,

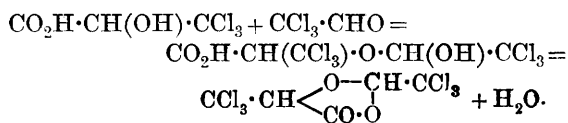
m. p. 117—118°, b. p. 212—213°/13 mm. (partial decomp.); *cis*- $\alpha$ -bromocinnamamide, m. p. 129°, b. p. 215—216°/13 mm. The  $\alpha$ -iodocinnamic acids (compare Bougault, A., 1916, i, 817) are obtained by the action of a solution of iodine in potassium iodide on the semicarbazone of phenylpyruvic acid in the presence of alkali, and are separated by taking advantage of the differences in their strengths; the *trans*-acid forms colourless leaflets, m. p. 162—163°, and yields a *methyl* ester, b. p. 132—133° (corr.)/0.4 mm., whilst the *cis*-acid forms yellow crystals, m. p. 110—111°, and gives a *methyl* ester, b. p. 114—115° (corr.)/0.4 mm. *Methyl trans*- $\beta$ -chlorocinnamate, m. p. 29°; *methyl cis*- $\beta$ -chlorocinnamate, m. p. 34°, b. p. 96—97° (corr.)/0.5 mm.; *methyl trans*- $\beta$ -bromocinnamate, colourless needles, m. p. 56°, b. p. 110—111°/0.6 mm.; *methyl trans*- $\alpha\beta$ -dichlorocinnamate, b. p. 121°/0.6 mm.; *methyl cis*- $\alpha\beta$ -dichlorocinnamate, b. p. 113°/0.6 mm., *methyl trans*- $\alpha\beta$ -dibromocinnamate, hexagonal rods, m. p. 64—65°, b. p. 138°/0.5 mm.; *methyl cis*- $\alpha\beta$ -dibromocinnamate, b. p. 124°/0.5 mm.

Attempts to obtain *cis*- $\beta$ -ethoxycinnamic acid are described. On one occasion a small amount of an acid, m. p. 78°, was isolated from the products of hydrolysis of ethyl  $\beta$ -ethoxycinnamate, which is possibly the desired substance, but the preparation could not be repeated. *trans*- $\beta$ -Ethoxycinnamic acid is extensively decomposed when its solution in benzene is exposed to ultra-violet light, ethoxystyrene being produced. Under similar treatment, the ethyl ester is considerably resinified, but on distillation of the product a fraction of lower boiling point was obtained which yielded an acid, m. p. 70—80° in small amount. Sodium  $\beta$ -ethoxycinnamate became completely resinified when illuminated. Similar observations with  $\beta$ -phenoxycinnamic acid and its ester are recorded. H. W.

**Optically Active Cinnamic Acids and the Cinnamates of Tartaric Acid which are Produced at the Formation of the Former.** EMIL ERLÉNMEYER and GUSTAV HILGENDORFF (*Biochem. Zeitsch.*, 1920, **103**, 79—123).—Tartaric acid was fused with cinnamoyl chloride, cinnamic anhydride, and cinnamic acid respectively at 168—170°. The cinnamic acid was extracted from the fused mass with light petroleum. The acid thus obtained was optically active. The highest activity was manifested by the cinnamic acid obtained by extracting the product of fusion of cinnamic anhydride with tartaric acid. The residues obtained by extracting the fused masses with light petroleum were further extracted with ether, yielding a colloidal fraction which was again fractionated either by extraction with benzene or by treating it with sodium carbonate, gradually acidifying, and extracting the successive fractions with ether. The various fractions thus obtained containing mixtures of cinnamates showed a carbon content varying from 55.76%, which represents the carbon content of the monocinnamates, to 64.39%, which is that of the dicinnamates. The lowest rotation was shown by the cinnamates obtained from the fusion

with cinnamic acid, the highest rotation by those obtained with cinnamoyl chloride. An intermediate value was shown by cinnamates from the anhydrides. This is explained by the presence of large quantities of the highly active dicinnamate in the chloride mixture and the absence of the less active monocinnamate, which is, however, present in the anhydride fusion and more so in the cinnamic acid fusion. A colloidal monodicinnamate ( $\alpha_D - 120^\circ$  approximately) was also obtained from the cinnamoyl chloride fusion. Cinnamates with a similar number of carbon atoms, but of a higher rotation, were obtained from the anhydride and from the cinnamic acid fusions. These masses also yielded a fraction of the same carbon content as the dicinnamates, but of a considerably lower rotation. It is suggested that the optical activity of the cinnamic acid extracted from the cinnamic anhydride fusion is due to the "induction" influence of the cinnamates formed. S. S. Z.

**Benzylic Acid and Aldehydes.** A. BISTRZYCKI and BRUNO BRENNEN (*Helv. Chim. Acta*, 1920, **3**, 468—472).—The authors have shown (see this vol., i, 630) that, whereas 1 mol. of thioglycollic acid condenses with 2 mols. of an aldehyde, 1 mol. of thio-benzylic acid condenses with only 1 mol. of an aldehyde. The experiments now described show that benzylic acid acts on aldehydes in the same way as aliphatic hydroxy-acids or thiobenzylic acid. According to Wallach (A., 1878, 288), the first stage in the formation of chloralide by the interaction of trichlorolactic acid and anhydrous chloral consists in the conversion of the acid into trichlorolactide, which then reacts with the chloral. The authors, however, consider it more probable that the reacting compounds first form an additive compound comparable with chloral alcoholate, decomposition with loss of water then taking place:



The *methylene ether ester of benzylic acid*,  $\text{CPh}_2 \begin{array}{c} \text{C}-\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{O} \end{array}$ , prepared by the interaction of benzylic acid and formaldehyde, forms transparent, rhomboidal plates often with truncated angles, softening a little below its m. p.,  $43-44^\circ$ . The powdered substance is converted into deep blue flocks by concentrated sulphuric acid, the latter turning first green and then colourless. It is appreciably more stable than the corresponding ester of glycollic acid (compare de Bruyn and van Ekenstein, A., 1902, i, 76; 1903, i, 149), from which it is derived.

The *benzylidene ether ester*,  $\text{CPh}_2 \begin{array}{c} \text{C}-\text{CHPh} \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{O} \end{array}$ , obtained from benzylic acid and benzaldehyde, crystallises in bundles of flat, microscopic prisms, m. p.  $94-95^\circ$ , and dissolves in concentrated sulphuric

acid, giving a violet-red solution, which shows a faint greenish-brown fluorescence. This compound also exhibits marked stability.

Attempts to couple acetone with benzylic acid were unsuccessful.

T. H. P.

**Derivatives of Gallic Acid. I. Synthesis of 4-Hydroxy-3:5-dimethoxyphthalic Acid.** RUPCHAND LILARAM ALIMCHANDANI and ANDREW NORMAN MELDRUM (T., 1920, 117, 964—970).

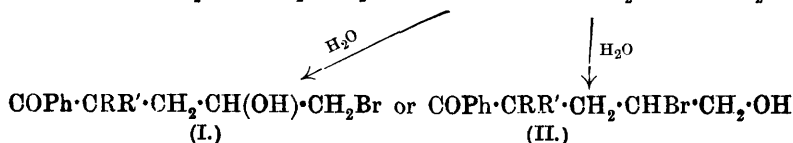
**Improved Process for the Elimination of Carboxyl Groups.** JAMES ERNEST MARSH (Brit. Pat. 144897).—Carboxyl groups may be eliminated from organic acids, particularly hydroxy-aromatic acids, such as gallic acid, by heating the acid with a dry metallic salt, preferably an alkali haloid. The reaction is advantageously carried out under reduced pressure, and, if the product is volatile, it may be conducted in a vacuum still, so that the decomposition of the acid and the recovery of the product by distillation proceed simultaneously. For instance, pyrogallol is obtained in a technically pure condition by distilling a mixture of gallic acid with half its weight of sodium chloride at 250° and 15 mm. pressure. The yield amounts to 95% of the theoretical.

G. F. M.

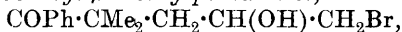
**Phenolphthalein.** F. UTZ (*Süddeut. Apoth. Zeit.*, 1920, 60, 430—431, 442—444; from *Chem. Zentr.*, 1920, iv, 155).—The amounts of phenolphthalein in grams contained in 100 c.c. of a warm saturated solution of the substance in the various solvents are as follows: ethyl alcohol, 20.91; methyl alcohol, 14.18; acetone, 26.39; chloroform, 3.06; carbon disulphide, 0.18; ether, 5.92; light petroleum, 0.18 or 1.06, depending on the boiling point of the solvent; benzene, 0.16; carbon tetrachloride, traces; xylene, 0.18; toluene, 0.61; nitrobenzene, 4.41; ethyl acetate, 6.57. Water (10 c.c.) dissolves 0.0002 gram of phenolphthalein at the ordinary temperature, and about ten times this amount when warmed.

H. W.

**Bromohydrins and Dibromo-derivatives obtained from the Alkylallylacetophenones,  $\text{COPh}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$  and  $\text{COPh}\cdot\text{CRR}'\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$ .** A. HALLER and (MME) P. RAMART-LUCAS (*Compt. rend.*, 1920, 171, 144—148).—The dialkylacetophenones studied when treated with bromine in chloroform solution give bromohydrins, the intermediate dibromo-derivatives being unstable and decomposed by moisture. The authors favour the constitution (formula I) for the  $\text{COPh}\cdot\text{CRR}'\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2 + \text{Br}_2 \rightarrow \text{COPh}\cdot\text{CRR}'\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$



bromohydrins obtained. Dimethylallylacetophenone in this way gives *ε*-bromo-*β*-benzoyl-*β*-methylpentan-*δ*-ol,



m. p. 106°.

Diethylallylacetophenone gives *ζ*-bromo-*γ*-benzoyl-*γ*-ethylhexan-*ε*-ol,  $\text{COPh} \cdot \text{C}(\text{Et})_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2\text{Br}$ , m. p. 84—88°.

Methylbenzylallylacetophenone gives *ε*-bromo-*β*-benzoyl-*β*-benzylpentan-*δ*-ol,  $\text{COPh} \cdot \text{CMeBz} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2\text{Br}$ .

Methylallylacetophenone under similar conditions gives a stable dibromo-derivative, *δ**ε*-dibromo-*β*-benzoylpentane,



m. p. 128°.

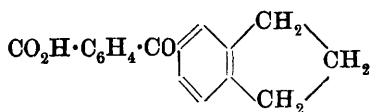
W. G.

**Benzo-polymethylene Compounds. I. Certain Regularities in Substitution.** JULIUS VON BRAUN, GEORG KIRSCHBAUM, and HANS SCHUHMAN (Ber., 1920, **53**, [B], 1155—1173).—The communication is the first of a series devoted to the study of substances containing an aromatic nucleus to which a saturated hydrocarbon chain is cyclically attached. The action of oxalyl chloride, acetyl chloride, phthalic anhydride, and diethylmalonyl chloride on benzopentamethylene (hydrindene), tetrahydronaphthalene, and tetrahydroacenaphthene has been investigated. The behaviour of the first is not completely similar to that of either *o*-xylene or naphthalene; tetrahydronaphthalene, in contrast to naphthalene, yields only uniform products instead of mixtures of isomerides, whilst tetrahydroacenaphthene gives a mixture of monobasic acids with oxalyl chloride.

Hydrindene and oxalyl chloride react in carbon disulphide solution in the presence of aluminium chloride to yield mainly hydrindene-*β*-carboxylic acid, m. p. 178—179° (chloride, b. p. 140—142°/12 mm., amide, m. p. 137—138°), the constitution of which is deduced from its oxidation by nitric acid at 140° to trimellitic acid; hydrindene-*α*-carboxylic acid appears to be formed in small amount as by-product. Tetrahydronaphthalene and oxalyl chloride give exclusively tetrahydronaphthalene-*β*-carboxylic acid, b. p. 216°/14 mm., m. p. 152—153°, which is readily hydrogenated by sodium and amyl alcohol to decahydronaphthalene-*β*-carboxylic acid, b. p. 190—192°/21 mm., m. p. 79°. Tetrahydronaphthalene-*β*-carboxyl chloride has b. p. 162°/13 mm., whilst the corresponding amide forms shining leaflets, m. p. 137—138°. Tetrahydroacenaphthene and oxalyl chloride yield a mixture of acids, which are separated by repeated crystallisation from alcohol; of these, the more sparingly soluble compound has m. p. 206° after softening at 200°, and is the main product. The isomeric acid has m. p. 170—180°, and has not been isolated in the pure state. Both isomerides yield benzene-1:2:3:4-tetracarboxylic acid when oxidised with nitric acid.

Acetyl chloride and hydrindene react readily, with formation of *β*-hydrindyl methyl ketone, b. p. 134—135°/11 mm. (semicarb-

*azone*, m. p. 229°, *oxime*, m. p. 114°;  $\beta$ -*hydrindyl bromomethyl ketone*, leaflets, m. p. 58—59°, which do not attack the mucous membrane;  $\beta$ -*hydrindyl dibromomethyl ketone*, m. p. 58—59°). The  $\beta$ -position of the acetyl group follows from the oxidation of the ketone by permanganate to hydrindene- $\beta$ -carboxylic acid, and

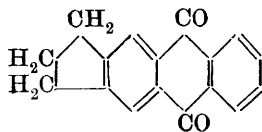


to an oily *acid*, which in all probability is  $\beta$ -hydrindoyl-formic acid, and is oxidised by nitric acid to trimellitic acid. Hydrindene and phthalic anhydride give exclusively

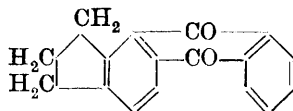
$\beta$ -*hydrindoylbenzoic acid* (annexed formula), m. p. 169°, which is converted by zinc dust in ammoniacal solution into the *acid*,

$\text{CH}_2 \langle \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \rangle \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , m. p. about 115°, but mainly

into the *lactone*,  $\text{CH}_2 \langle \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \rangle \text{C}_6\text{H}_3 \cdot \text{CH} \langle \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{O} \end{smallmatrix} \rangle \text{CO}$ , m. p. 154°. It is decomposed with unusual difficulty by molten potassium hydroxide to yield hydrindene- $\beta$ -carboxylic acid. When dehydrated by fuming sulphuric acid, it gives a mixture of *hydrindanthraquinones*, delicate, matted needles, m. p. 180—181°, and yellow, crystalline powder, m. p. 108—110°. The formulæ

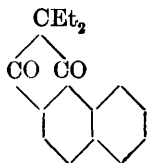


(I.)



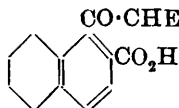
(II.)

I and II are assigned to these respectively, since the former, on treatment with zinc and ammonia, gives *hydrindanthracene*, m. p. 242—243°, whilst the latter only yields readily soluble products of lower melting point, from which a definite substance could not be isolated.



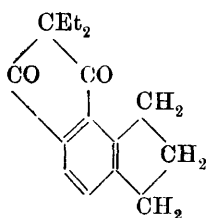
Tetrahydronaphthalene and diethylmalonyl chloride yield exclusively the *diethylindandione* derivative (annexed formula), b. p. 207—211°/15 mm., m. p. 56—57°, which is oxidised by nitric acid to benzene-1:2:3:4-tetracarboxylic acid, m. p.

238°. Concentrated potassium hydroxide solution transforms the diketone into an *acid*, m. p. 135°, which probably has the annexed constitution. Reduction of the diketone with



amalgamated zinc and hydrochloric acid leads to the formation of the corresponding *hydrocarbon*, mobile oil, b. p. 164—166°/11 mm., which, however, is not completely free from oxygen; the latter can be totally eliminated by prolonging the duration of reduction, but, under these conditions, the hydrindene ring is ruptured, and the product is  $\gamma$ -methyl- $\gamma$ -

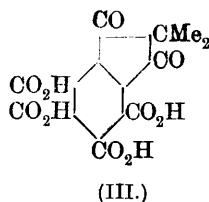
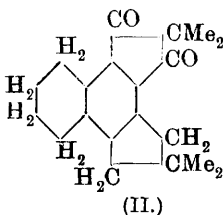
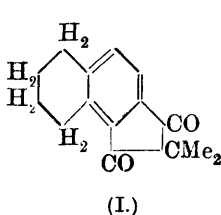




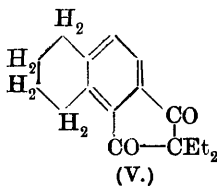
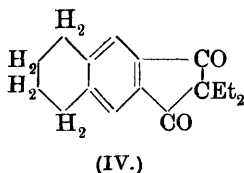
*ethylbutyltetrahydronaphthalene*, b. p. 141—144°/11 mm., which is oxidised by nitric acid to trimellitic acid. Diethylmalonyl chloride reacts with hydrindene in a precisely analogous manner, yielding the *product* (annexed formula), pale yellow, rather viscous oil, b. p. 186—191°/13 mm., which is oxidised by nitric acid to mellophanic acid, m. p. 238°. H. W.

**Derivatives of *ac*-Tetrahydronaphthalene and of Tetrahydroacenaphthene.** KARL FLEISCHER and FRITZ SIEFERT (*Ber.*, 1920, **53**, [B], 1255—1261).—The action of substituted malonyl chlorides on partly hydrogenated aromatic hydrocarbons has been investigated by Fleischer (*Zeitsch. angew. Chem.*, 1919, **32**, [ii], 596; 1920, **33**, [ii], 160). Since the same subject is also engaging the attention of von Braun (preceding abstract), the authors give an account of their work with *ac*-tetrahydronaphthalene and tetrahydroacenaphthene, but reserve the full experimental details for a later publication.

Dimethylmalonyl chloride and tetrahydronaphthalene yield exclusively 2:2-dimethyltetrahydronaphth- $\alpha\beta$ -indane-1:3-dione (I), m. p. 75°, which is hydrolysed to 1-isobutyryltetrahydro-



*naphthalene-2-carboxylic acid*, m. p. 120°; the latter is oxidised by nitric acid to 2:2-dimethylbenzindane-1:3-dione-6:7-dicarboxylic acid. The indanedione is reduced by amalgamated zinc and hydrochloric acid to 2:2-dimethyltetrahydronaphth- $\alpha\beta$ -hydrindene, b. p. 156°/18 mm. The  $\alpha\beta$ -position of the hydrindene ring in the hydrocarbon molecule is established by its conversion by dimethylmalonyl chloride into 2:2:5:5-tetramethyltetrahydronaphthdihydrindane-4:6-dione (II), m. p. 148—149°, which is reduced to 2:2:5:5-tetramethyltetrahydronaphthdihydrindene, m. p. 105—106°, and is oxidised by nitric acid to a tetracarboxylic acid (III), decomposing at 277°, and mellitic acid.



With diethylmalonyl chloride and tetrahydronaphthalene, both isomerides are formed; 2:2-diethyltetrahydronaphth- $\beta\beta$ -indane-1:3-dione (IV) has m. p.  $118^\circ$ , whilst 2:2-diethyltetrahydronaphth- $\alpha\beta$ -indane-1:3-dione (V) has m. p.  $54-55^\circ$ . Only the second of these yielded a well-defined acid, m. p.  $134-135^\circ$ , on hydrolysis. The former dione is oxidised by nitric acid to pyromellitic acid, whilst the latter gives 2:2-diethylbenzindane-1:3-dione-6:7-dicarboxylic acid, m. p.  $174-176^\circ$ . The diones are completely reduced by amalgamated zinc and hydrochloric acid to 2:2-diethyltetrahydronaphth- $\beta\beta$ -hydrindene, m. p.  $49^\circ$ , and 2:2-diethyltetrahydronaphth- $\alpha\beta$ -hydrindene, b. p.  $163-165^\circ/12$  mm., respectively.

[With WILHELM ECKERT.]—2-Acetyltetrahydronaphthalene is reduced to 2-ethyltetrahydronaphthalene, b. p.  $127^\circ/21$  mm., from which, by regulated acetylation and subsequent reduction, 2:3-diethyltetrahydronaphthalene, b. p.  $150-151^\circ/18$  mm., and 1:2:3-triethyltetrahydronaphthalene, b. p.  $165-172^\circ/23$  mm., are successively prepared.

Tetrahydroacenaphthene is transformed by diethylmalonyl chloride into 2:2-diethyltetrahydroacenaphth- $\alpha\beta$ -indane-1:3-dione (annexed formula), m. p.  $88-89^\circ$ , which is reduced by amalgamated zinc and hydrochloric acid to 2:2-diethyltetrahydroacenaphth- $\alpha\beta$ -hydrindene, b. p.  $190-195^\circ/16$  mm. The dione is oxidised to a mixture of benzenepentacarboxylic acid and diethylbenzindane-1:3-dione-4:5:6-tricarboxylic acid.

H. W.

**Menthol and Phenylhydrazine Derivatives of the Higher Fatty Acids.** D. H. BRAUNS (*J. Amer. Chem. Soc.*, 1920, **42**, 1478—1481).—The menthyl esters and phenylhydrazine derivatives of certain of the higher fatty acids were prepared in an attempt to find a means of estimating the amounts of individual acids present in mixtures. This aim was not fulfilled. The menthyl esters prepared by heating the acid chlorides with menthol were menthyl laurate,  $D_4^{20}$  0.8915,  $[\alpha]_D^{20} -46.07^\circ$ ; menthyl myristate, m. p.  $21-22^\circ$ ,  $D_4^{20}$  0.882,  $[\alpha]_D^{20} -42.33^\circ$  (compare Hilditch, T., 1912, **101**, 192); menthyl palmitate, m. p.  $32^\circ$ ,  $D_4^{20}$  0.8848,  $[\alpha]_D^{20} -39.10^\circ$ ; menthyl stearate, m. p.  $38-39^\circ$ ,  $D_4^{25}$  0.8665,  $[\alpha]_D^{25} -36.60^\circ$ ; menthyl arachidate, m. p.  $55^\circ$ ,  $D_4^{25}$  0.8566,  $[\alpha]_D^{25} -30.63^\circ$ . All these rotations were determined directly on the molten substances. The phenylhydrazides, prepared by heating the acids with excess of phenylhydrazine, were palmitic phenylhydrazide, m. p.  $105^\circ$ ; stearic phenylhydrazide, m. p.  $110-111^\circ$ ; arachidic phenylhydrazide, m. p.  $108-109^\circ$ .

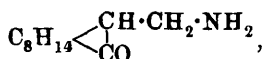
W. G.

**“Cresineol,” a Compound of Cineole and o-Cresol.** T. TUSTING COCKING (*Pharm. J.*, 1920, **105**, 81).—When one molecule of cineole is mixed with one molecule of o-cresol, heat is developed, and a crystalline substance separates as the mixture

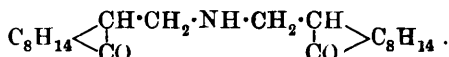
cools. The name "cresineol" is given to the substance. It has m. p.  $55.2^{\circ}$ , b. p.  $186.5-189^{\circ}$ ,  $D_{20}^{60}$  0.9661, and  $n_D^{60}$  1.4846; it is soluble in most organic solvents, and is decomposed by alkali hydroxides into its constituents. W. P. S.

**Dependence of Optical Rotatory Power on Chemical Constitution. II. The Effect of Position-isomerism and Conjugation on Optical Activity among Aryl Derivatives of Amino- and Bisimino-camphor.** BAWA KARTAR SINGH, DALIP SINGH, GURU DUTT, and GOPAL SINGH (T., 1920, 117, 980-988).

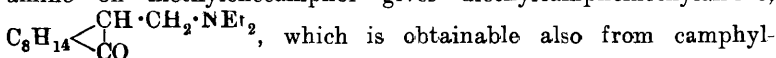
**Reduction Products of Hydroxymethylenecamphor. IV. Coupling of Bases with Methylenecamphor.** HANS RUPE and WALTER KUSSMAUL (*Helv. Chim. Acta*, 1920, 3, 515-540. Compare A., 1919, i, 335).—Unsuccessful attempts have been made to prepare the methylcamphoramine of the structure,



(1) by treating camphylbromomethane with ammonia, and (2) by reduction of aminomethylenecamphor. Reaction (1) yields a compound which forms a nitrosoamine, a benzoyl derivative and a phenylthiocarbamide derivative, and may be obtained also by reduction with aluminium amalgam in neutral solution of the imide described by Bishop, Claisen, and Sinclair (A., 1895, i, 62); this compound is evidently di(camphomethyl)-amine,

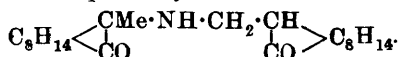


The latter is obtained also when methylenecamphor is treated with ammonia in a sealed tube, and when camphylcarbinol and ammonia react under pressure. Derivatives of the methylcamphoramine sought may, however, be obtained. Thus, the action of diethylamine on methylenecamphor gives diethylcamphomethylamine,



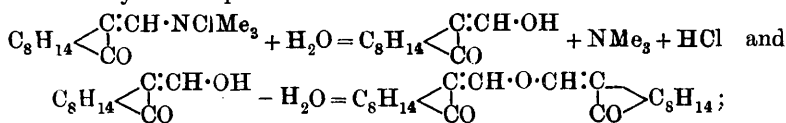
which is obtainable also from camphylbromomethane and diethylamine.

Reduction of aminomethylenecamphor by means of aluminium amalgam gives in small yield a base which is isomeric with, and exhibits quite similar behaviour to, the secondary base obtained by reaction (1), and is probably of the structure



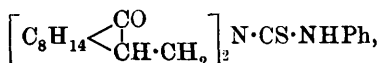
Attempts were also made to prepare the desired methylcamphoramine by reducing methylenecamphoramide with hydrogen in presence of nickel, by means of camphylbromomethane and phthalimide, and from the amide of camphorylacetic acid (compare Rupe, Warder, and Takagi, A., 1919, i, 27), but in no case successfully.

Various quaternary ammonium compounds derived from methylene- and methyl-camphor are described. Noteworthy is the formation of the anhydride of hydroxymethylenecamphor (compare Bishop, Claisen, and Sinclair, *loc. cit.*) by treatment with sodium hydroxide of the quaternary base obtained from trimethylamine and methylenecamphor chloride:



the trimethylamine liberated acts as the dehydrating agent.

*Di(camphomethyl)-amine*,  $(\text{C}_{11}\text{H}_{17}\text{O})_2\text{NH}$ , forms an amorphous, crumbly, white mass of faintly basic odour, m. p.  $124^\circ$ , and decomposes on distillation even under reduced pressure. The *hydrobromide*,  $(\text{C}_{11}\text{H}_{17}\text{O})_2\text{NH}\cdot\text{HBr}$ , slender, white leaflets, sintering and blackening at  $285^\circ$ , and remaining unmelted at  $350^\circ$ ; the *hydrochloride*, thin, white leaflets or felted needles with a persistent, bitter taste, sintering and blackening at  $270^\circ$ , and remaining unmelted at  $350^\circ$ ; the *platinichloride*, quadratic leaflets, boiling suddenly and blackening at  $240^\circ$ ; the *oxalate* (normal), microscopic, rectangular leaflets, decomposing at  $191\text{--}192^\circ$ ; the *nitrosoamine*,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CH}\cdot\text{CH}_2\cdot\text{N}(\text{NO})\cdot\text{CH}_2\cdot\text{CH} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ \text{CO} \quad \text{CO} \end{array} \text{C}_8\text{H}_{14}$ , slender, white needles, softening at  $100^\circ$ , m. p.  $106^\circ$ ; and the *benzoyl* derivative,  $\text{C}_{29}\text{H}_{39}\text{O}_3\text{N}$ , bundles of slender needles, m. p.  $132^\circ$ , were prepared. *Di(camphomethyl)-phenylthiocarbamide*,



forms slender, silky needles, m. p.  $160\text{--}161^\circ$ , and is sometimes accompanied by an *isomeride*, m. p.  $129\text{--}130^\circ$ .

The *base*,  $\text{C}_{22}\text{H}_{35}\text{O}_2\text{N}$ , obtained by reducing aminomethylenecamphor by means of aluminium amalgam, forms a friable mass, softening at  $130^\circ$ , m. p.  $145\text{--}146^\circ$ . The following derivatives were prepared: *hydrochloride*, slender, rectangular leaflets, neither melting nor decomposing; *platinichloride*, decomposing at  $230^\circ$ ; *oxalate*, glittering leaflets, softening at  $250^\circ$ , m. p.  $258^\circ$  (decomp.); *nitrosoamine*,  $\text{C}_{22}\text{H}_{34}\text{O}_3\text{N}_2$ , crystalline powder, softening at  $158^\circ$ , m. p.  $164^\circ$ .

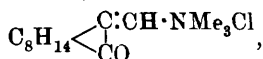
Reduction of methylenecamphorimide by means of aluminium amalgam yields methylcamphor, di(camphomethyl)-amine, and a *base*, giving an oxalate, m. p.  $248\text{--}250^\circ$ .

Similar reduction of ethyl methylenecamphor-*p*-aminobenzoate yields ethyl *p*-aminobenzoate, together with a *compound*,  $\text{C}_{26}\text{H}_{25}\text{O}_3\text{N}$  or  $\text{C}_{26}\text{H}_{23}\text{O}_2\text{N}$ , crystallising in small prisms, m. p.  $278\text{--}279^\circ$ .

*Diethylcamphomethylamine*,  $\text{C}_{15}\text{H}_{27}\text{ON}$ , is a pale yellow, oily liquid of faintly basic odour, b. p.  $137.5^\circ/8.5\text{ mm}$ . The *hydrochloride*, slender, white needles, m. p.  $167\text{--}168.5^\circ$ , giving a bitter,

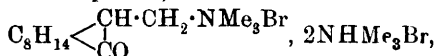
aqueous solution, and the *platinichloride*, slender, salmon-coloured needles, m. p.  $194^{\circ}$ , decomposing at  $212^{\circ}$ , were prepared.

*Methylenecamphor*trimethylammonium chloride,



prepared from methylenecamphor chloride and trimethylamine, forms vitreous, quadratic, deliquescent plates, m. p.  $162^{\circ}$ , and yields intensely bitter, aqueous solutions. With sodium hydroxide, the aqueous solution of the chloride yields trimethylamine, and, on subsequent acidification, hydroxymethylenecamphor; when heated in a reflux apparatus on a boiling-water bath, it gives the anhydride of hydroxymethylenecamphor.

Methylcamphortrimethylammonium chloride could not be prepared, but the corresponding bromide, obtained from camphylbromomethane and trimethylamine, forms with trimethylamine hydrobromide the compound,



which crystallises in colourless leaflets, softening at  $183^{\circ}$ , melting at  $192^{\circ}$ , again solidifying and melting a second time, and boiling at  $286^{\circ}$ .

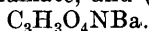
T. H. P.

**Essential Oil of *Mosta grosseserrata*, Maxim.** YOSHIATSU MURAYAMA (*J. Pharm. Soc. Japan*, 1920, 389—408. Compare Furukawa and Tomizawa, *J. Chem. Ind. Japan*, 1919, **22**, 383).—Three specimens of the essential oil from the wild plant contained: (1) thymol, methyleugenol, *p*-cymene, a terpene, and a sesquiterpene, b. p.  $136^{\circ}/12$  mm.; (2) thymoquinol; (3) myristicin. The oil from the cultivated plant contained thymoquinol, thymol, and a terpene.

K. K.

**Hiptagin, a New Glucoside from *Hiptage madablota*, Gaertn.** K. GORTER (*Bull. Jard. bot. Buitenzorg*, 1920, [iii], **2**, 187—202).—This glucoside is extracted in a yield of 8% from the root bark by acetone or ethyl acetate. The bark of the stem contains much less. *Hiptagin*,  $\text{C}_{10}\text{H}_{14}\text{O}_9\text{N}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ , forms silky needles, m. p.  $110^{\circ}$ ,  $[\alpha]_D + 3.5^{\circ}$  in 5% acetone solution. The most characteristic chemical property is the formation by dilute alkali hydroxide, even in the cold, of ammonia and hydrocyanic acid. Dilute acids act quite differently, forming dextrose, and, at the same time, breaking down the genin in various ways; 5% aqueous sulphuric acid at  $100^{\circ}$  forms tartronic acid. Concentrated hydrochloric acid, mixed with 4 volumes of acetone, forms in five days at the ordinary temperature strong, monobasic *hiptagenic acid*,  $\text{C}_3\text{H}_5\text{O}_4\text{N}$ , needles, m. p.  $68^{\circ}$ ,  $k = 1.20 \times 10^{-4}$ , giving crystalline silver, lead, and zinc salts. The hypothetical hiptagenin is decomposed according to the equation  $\text{C}_4\text{H}_4\text{O}_4\text{N}_2 + 2\text{H}_2\text{O} = \text{C}_3\text{H}_5\text{O}_4\text{N} + \text{CO}_2 + \text{NH}_3$ . Hiptagenic acid is also formed by destructive distillation of the glucoside, and is regarded as having the constitution  $\text{OH} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}(\text{OH}) : \text{CH} \cdot \text{OH}$ . By heating hiptagenic acid

with hydrochloric acid on the water-bath, it is hydrolysed to diglycollic and formic acids and to hydroxylamine hydrochloride,  $2\text{C}_3\text{H}_5\text{O}_4\text{N} + 3\text{H}_2\text{O} = \text{C}_4\text{H}_6\text{O}_5 + 2\text{HCO}_2\text{H} + 2\text{NH}_2\cdot\text{OH}$ . Sodium ethoxide at the ordinary temperature decomposes hiptagin, with the formation of sodium nitrite, but hiptagenic acid is only slowly hydrolysed by boiling alcoholic sodium ethoxide solution, probably with the formation of formhydroxamic acid (red coloration with ferric chloride) and of glyoxal,  $\text{OH}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{CO}\cdot\text{NH}\cdot\text{OH} = \text{OH}\cdot\text{CH}\cdot\text{N}\cdot\text{OH} + \text{CHO}\cdot\text{CHO}$ . The action of aqueous alkalis on hiptagenic acid is very complex. The best results were obtained by heating with barium hydroxide at  $50^\circ$ , which formed barium nitrite, barium formhydroxamate, and (in 72% yield) a salt,



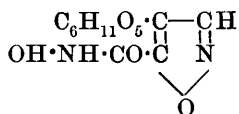
The latter is regarded as derived from a carbamic acid,



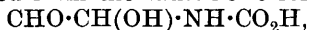
isomeric with hiptagenic acid. On heating with phosphoric acid, the barium salt gives half a molecular proportion of carbon dioxide, hydrocyanic and oxalic acids, ammonia, formaldehyde, and glyoxal. The isomerisation of hiptagenic to the carbamic acid is compared to the Beckmann transformation of oximes. The carbamic acid may be decomposed on the one hand to ammonia and glyoxal, and on the other to formaldehyde, water, and cyanofornic acid. The last-named may yield hydrocyanic acid and carbon dioxide, or oxalic acid and ammonia. Glyoxal and formaldehyde were obtained as *p*-nitrophenylhydrazones.

The action of barium hydroxide on hiptagin takes place according to the equation  $\text{C}_{10}\text{H}_{14}\text{O}_9\text{N}_2 + 3\text{H}_2\text{O} = \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_3\text{H}_5\text{O}_4\text{N} + \text{CO}_2 + \text{NH}_3$ . The barium salt of the carbamic acid here has the

composition  $(\text{C}_3\text{H}_4\text{O}_4\text{N})_2\text{Ba}$ , and appears to



be derived from the tautomeric form,



without the two acid hydroxymethylene groups formulated above for the salt from hiptagenic acid. The author proposes for

hiptagin the annexed formula of an *isooxazole* derivative. He considers that it is formed in the plant by reduction of nitrates to hydroxylamine, and condensation of this base with aldehydes and ketones.

G. B.

### Synthesis of Aromatic Amino-acids in the Living Cell.

L. HUGOUNENQ and GABRIEL FLORENCE (*Bull. Soc. chim. Biol.*, 1920, **2**, 133—136).—Aspergillin, the black pigment of *Aspergillus niger*, previously described by Linossier (A., 1891, 751, 1089), is prepared by extracting the spores with cold 10% sodium hydroxide. The extract, on being neutralised with sulphuric acid, produces a flocculent, black precipitate of the pigment in a more or less pure condition. After purification, the product forms a shining, amorphous powder, insoluble in water and in acids, but very soluble in alkalis. It contains 4.97% of ash, in which were present iron, sulphur, zinc, and calcium. Elementary analysis gave the percentage figures: C 43.5, H 6.9, N 12.6, P 8.7, Fe 0.455,

Ca 0.352, Mg 0.126, S 0.57, O 27.367. It appears to contain an indole ring in the molecule.  
J. C. D.

**Henna (*Lawsonia inermis*). Chemical Constitution of Lawsone.** II. G. TOMMASI (*Gazzetta*, 1920, 50, i, 263—272).—Lawsone, the colouring matter contained in henna leaves (compare *Ann. R. Staz. Chim. agr. sper. Roma*, 1920, 10), forms crystals, m. p. 192—195° (decomp.), and gives an orange-yellow, aqueous solution, which undergoes change when boiled. It is fixed well by wool and silk, and, rapidly and tenaciously, by the skin. In aqueous solutions of alkali or alkaline earth hydroxides, or in concentrated sulphuric acid, it dissolves, giving a bright orange-red coloration. In aqueous-alcoholic solution it gives: with ferric chloride, a reddish-brown precipitate; with stannous chloride or alum, a yellow precipitate; with copper acetate, an orange precipitate; with silver nitrate, an orange-red precipitate; with tannin it remains unchanged.

Its composition and its ebullioscopic behaviour in alcohol indicate the formula  $C_{10}H_6O_3$ , and it is distinctly acid in character and contains no methoxyl groups. The calcium salt,  $Ca(C_{10}H_5O_3)_2$ , forms silky, red needles. The acetyl derivative,  $C_{10}H_5O_2 \cdot OAc$ , crystallises in shining needles, m. p. 128—130°. When reduced by means of zinc dust and acetic acid, it is converted into a colourless leuco-derivative, which is readily oxidised to the original compound by atmospheric oxygen. By treatment with acetic anhydride and zinc dust, it is transformed into the compound,  $C_{16}H_{14}O_6$ , which crystallises in nacreous, white laminae, m. p. 133—134°. The conclusion is drawn that the molecule of lawsone contains one phenolic hydroxylic oxygen atom and two quinonic oxygen atoms. Further, since, in alcoholic solution, lawsone gives with nickel acetate an intense red coloration, and after some hours a deposit of garnet-red crystals (compare Brissemoret and Combes, A., 1907, ii, 411), the substance must be regarded as a hydroxy-naphthaquinone, and is probably identical with 2-hydroxy-1:4-naphthaquinone.  
T. H. P.

**Formation of Melanin.** J. VERNE (*Compt. rend. Soc. Biol.*, 1920, 83, 760—762; from *Chem. Zentr.*, 1920, iii, 156).—The brown dye, which has been proved histologically to be converted into melanin, is completely soluble in warm water, alkaline and acid solutions, and in formalin, but quite insoluble in alcohol and solvents for fats. The aqueous solution is faintly acidic, does not give the biuret or purine reactions, dissolves cupric hydroxide, and is readily diazotised. Addition of neutral formalin renders the solution strongly acidic. Addition of solutions of tyrosinase causes rapid blackening. Millon's reaction is strongly marked. The dye consists of polypeptides in which tyrosine is present, and is classed as an amino-acid dye. A considerable portion of the nitrogen, which can be titrated with formalin, disappears during the formation of melanin, whilst the total nitrogen remains unchanged.

H. W.

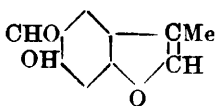
**The Constitution of Catechin. I. MAXIMILIAN NIERENSTEIN**  
(T., 1920, 117, 971—979).

**Syntheses in the Bergaptene Group.** P. KARRER, A. GLATTFELDER, and FR. WIDMER (*Helv. Chim. Acta*, 1920, 3, 541—558).—Condensation of 5-hydroxy-2-methylcoumarone with hydrocyanic acid and hydrogen chloride yields 5-hydroxy-2-methylcoumarone-4-aldimide hydrochloride, and the latter, when boiled with water, yields an aldehyde which is to be investigated later, but is most probably 5-hydroxy-2-methylcoumarone-4-aldehyde. When heated with acetic anhydride and sodium acetate, this aldehyde yields an "intermediate compound," which is converted when boiled with distilled water into 5-hydroxy-2-methylcoumarone-4-acrylic acid; treatment of the latter with methyl sulphate in concentrated alkaline solution yields 5-methoxy-2-methylcoumarone-4-acrylic acid, whilst in faintly alkaline solution methyl 5-methoxy-2-methylcoumarone-4-acrylate is obtained. The acrylic acid is highly stable, and shows not the slightest tendency to undergo dehydration to the corresponding coumarin; similarly, 5-hydroxy-4-chloroacetyl-2-methylcoumarone exhibits no tendency to ring-formation with loss of hydrogen chloride, the phenomenon in both cases being probably due to steric hindrance.

In order to exclude the influence of the methyl group of the furan ring and to approach more closely to the natural products, bergaptene and xanthotoxin, coumarone-coumarin derivatives free from methyl groups have been prepared. 5-Hydroxycoumarone is obtainable with difficulty from 7-acetoxycoumarin (compare Pechmann, A., 1884, 1173) by way of the dibromide and 5-hydroxycoumarone-1-carboxylic acid. 5-Hydroxycoumarone reacts with hydrocyanic acid and hydrogen chloride, giving 5-hydroxycoumarone-4-aldimide hydrochloride, which is converted on hydrolysis with hot water into 5-hydroxycoumarone-4-aldehyde. Like the methylated compounds mentioned above, this aldehyde is not converted into the coumarin expected when boiled with acetic anhydride and sodium acetate.

The methyl ether of phloroglucinol undergoes condensation with ethyl acetoacetate and sodium, yielding an ethyl methoxyhydroxymethylcoumaronecarboxylate. Cautious sublimation of the corresponding free acid gives the methoxymethylcoumarone, in which the closure of the coumarone ring takes place in either the ortho- or the para-position to the methoxyl group of the benzene nucleus.

5-Hydroxy-2-methylcoumarone-4-aldehyde (annexed formula), crystallises in pale yellow needles, m. p. 181°, and in alcoholic solution gives a green coloration with ferric chloride. The *oxime*,  $C_{10}H_9O_3N$ , forms long, white needles, m. p. 186° (decomp.), the *anil*,  $C_{16}H_{13}O_3N$ , yellow or yellowish-brown needles, m. p. 160° (decomp.), and the *phenylhydrazone*, yellow crystals, m. p. 165° (decomp.).





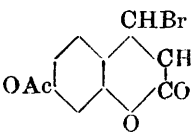
The intermediate compound (see above) forms small, yellow crystals, m. p.  $114^{\circ}$ , and is insoluble in sodium carbonate, hydrogen carbonate, or hydroxide solution.

5-Hydroxy-2-methylcoumarone-4-acrylic acid (annexed formula) crystallises in shining, pale yellow needles, m. p.  $199^{\circ}$ , sublimes partly at a higher temperature, dissolves readily in alkali solutions, and in acetone solution decolorises permanganate.

5-Methoxy-2-methylcoumarone-4-acrylic acid,  $C_{13}H_{12}O_4$ , forms pale yellow needles, m. p.  $209^{\circ}$ , and dissolves readily in alkali solution. Its methyl ester,  $C_{14}H_{14}O_4$ , crystallises in yellow needles, m. p.  $216^{\circ}$ .

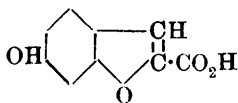
5-Hydroxy-2-methylcoumaran-4-aldehyde (annexed formula), prepared by the action of boiling water on the aldimide hydrochloride obtained by condensing 5-hydroxy-2-methylcoumaran (A., 1919, i, 595) with hydrocyanic acid and hydrogen chloride, crystallises in needles, m. p.  $185^{\circ}$ . The oxime,  $C_{10}H_{11}O_3N$ , m. p.  $190^{\circ}$  (decomp.), the anil, and the hydrazone were prepared.

5-Hydroxy-2-methylcoumaran-4-acrylic acid (annexed formula), prepared by boiling the preceding compound with acetic anhydride and sodium acetate, crystallises in pale yellow needles, m. p.  $208^{\circ}$ . In this case also no compound of coumarin character could be obtained.

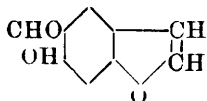
7-Acetoxycoumarin dibromide, , forms white leaflets, m. p.  $114^{\circ}$  (frothing).

5-Hydroxycoumarone-1-carboxylic acid (5-hydroxycoumarilic acid) (annexed formula), prepared by the action of alcoholic potassium hydroxide on the preceding compound, crystallises in microscopic leaflets, m. p.  $234-236^{\circ}$  (uncorr.) (decomp.), gives a brown coloration in alcoholic solution with ferric chloride, and dissolves in aqueous alkali to a solution showing blue fluorescence, which disappears when the liquid is boiled.

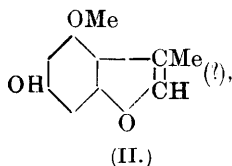
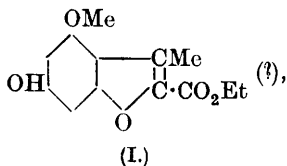
5-Hydroxycoumarone, obtained by rapid distillation of 5-hydroxycoumarilic acid with calcium oxide, forms long, flat needles, m. p.  $56^{\circ}$ , dissolves readily in alkali solution, quickly decolorises permanganate in acetone solution, gives a green coloration in alcoholic solution with ferric chloride, and is resinified with a red coloration by concentrated sulphuric acid.



**5-Hydroxycoumarone-4-aldehyde** (annexed formula) forms white crystals, decomposes without melting at  $260^{\circ}$ , and in alcoholic solution gives a canary-yellow coloration with aniline hydrochloride. When boiled with acetic anhydride and sodium acetate it yields a compound which has not the composition of a simple coumarone-coumarin.



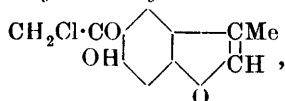
**Ethyl hydroxymethoxymethylcoumaronecarboxylate** (I), forms



crystals, m. p.  $230^{\circ}$ . The corresponding *acid* forms a white precipitate, m. p.  $202^{\circ}$  (decomp.).

**Hydroxymethoxymethylcoumarone** (II) is obtained as a white sublimate, m. p.  $75^{\circ}$  (previous softening), and has the odour of coumarone.

**5-Hydroxy-4-chloroacetyl-2-methylcoumarone**,



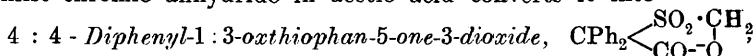
obtained from 5-hydroxy-2-methylcoumarone and chloroacetonitrile, forms crystals, m. p.  $192^{\circ}$ , and dissolves readily in dilute sodium hydroxide solution. T. H. P.

**3 : 6-Tetramethyldiaminoselenopyronine.** M. BATTEGAY and G. HUGEL (*Bull. Soc. chim.*, 1920, [iv], **27**, 557—560).—A mixture of sodium selenite and sulphuric acid is added gradually to sulphuric acid containing 25% of sulphur trioxide and at the same time tetramethyldiaminodiphenylmethane is added in small portions, so that it is always present in slight excess, the temperature not being allowed to rise above  $35^{\circ}$ . After an hour and a-half the mixture is poured on to ice, filtered, and a solution of zinc chloride added to the filtrate. The *zincchloride* of *tetramethyldiaminoselenopyronine*,  $C_{17}H_{19}N_2Cl_2Se \cdot ZnCl_2$ , is obtained in a crystalline form. It dissolves in sulphuric acid to a red solution, which on dilution with water turns blue. The addition of sodium hydroxide to this solution precipitates a reddish-blue base, which is soluble in ether. The colouring matter gives slightly soluble iodides and nitrates and insoluble dichromates. W. G.

**Synthesis of Derivatives of 1 : 3-Oxthiophan.** A. BISTRZYCKI and BRUNO BRENNEN (*Helv. Chim. Acta*, 1920, **3**, 447—467).—The behaviour of thiobenzyllic acid ( $\alpha$ -mercaptodiphenylacetic acid) (com-

pare Becker and Bistrzycki, A., 1915, i, 245) towards aldehydes, ketones, and ketonic acids is found to be analogous to that of thio-glycollic acid (Bongartz, A., 1886, 937; 1888, 478) and  $\alpha$ -thiolactic acid (Holmberg and Mattisson, A., 1907, i, 475) towards these carbonylic compounds.

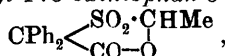
4:4-Diphenyl-1:3-oxthiophan-5-one (methylene ether ester of thiobenzyllic acid),  $\text{CPh}_2 \begin{smallmatrix} \text{S} - \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{O} \end{smallmatrix}$ , prepared by the interaction of formaldehyde and thiobenzyllic acid, crystallises in flat prisms or rhombic or triangular plates, m. p. 99—100°. Alkali carbonate or hydroxide decomposes it with formation of thiobenzyllic acid, whilst with ammonia solution it yields diphenylacetamide and diphenylacetic acid. It is not changed by concentrated hydrochloric acid at 100°, but dissolves gradually in concentrated sulphuric acid to a yellow solution, which becomes deep violet after a few minutes or more rapidly on heating. It is not attacked by bromine in boiling chloroform solution. By zinc dust and boiling acetic acid it is decomposed, yielding thioformaldehyde (?) and diphenylacetic acid, whilst chromic anhydride in acetic acid converts it into



which crystallises in glistening, quadrilateral leaflets or flat prisms, m. p. 92—94°, and with concentrated sulphuric acid yields a cupric blue solution deepening considerably in colour when heated. When a solution of the sulphone in dilute, boiling alkali hydroxide is rendered acid with hydrochloric acid, it yields sulphur dioxide and a white, flocculent precipitate.

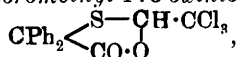
4:4-Diphenyl-2-methyl-1:3-oxthiophan-5-one,  $\text{CPh}_2 \begin{smallmatrix} \text{S} - \text{CHMe} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{O} \end{smallmatrix}$ , prepared from acetaldehyde and thiobenzyllic acid, forms microscopic, colourless, four-sided plates, often in bundles, m. p. 89—91°, and behaves towards concentrated sulphuric acid similarly to its lower homologue.

4:4-Diphenyl-2-methyl-1:3-oxthiophan-5-one-3-dioxide,



obtained on oxidising the preceding compound, exists in two modifications, which are possibly stereoisomerides related in the manner indicated by Hinsberg (A., 1916, i, 725; 1917, ii, 173, 461). The  $\alpha$ -form crystallises in colourless plates, m. p. 79—81°, and dissolves in hot concentrated sulphuric acid with formation of a reddish-brown solution with a violet reflexion. The  $\beta$ -form, obtained along with the  $\alpha$ -form or by treating the latter with boiling acetic acid, crystallises in colourless, microscopic rhombohedra, m. p. 97—98°.

4:4-Diphenyl-2-trichloromethyl-1:3-oxthiophan-5-one,



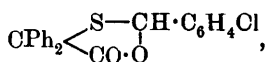
prepared from chloral and thiobenzyllic acid, forms colourless, pris-

matic plates, m. p. 107°. In hot concentrated sulphuric acid it dissolves with emission of an intense garlic odour and formation of a violet solution, turning first blue and then an indistinct green.

2:4:4-Triphenyl-1:3-oxthiophan-5-one,  $\text{CPh}_2 \begin{smallmatrix} \text{S}-\text{CHPh} \\ \text{CO}\cdot\text{O} \end{smallmatrix}$ , obtained from benzaldehyde and thiobenzyllic acid, forms colourless, mostly hexagonal plates, m. p. 94—96°. With ammonia solution at 125° it gives a small yield of a compound, m. p. 163—165°, of unknown character. It is not attacked by concentrated hydrochloric acid at 100°, but with aniline it furnishes an additive compound,  $\text{C}_{21}\text{H}_{16}\text{O}_2\text{S}\cdot\text{NH}_2\text{Ph}$ , which crystallises in bundles of colourless plates, softening at 67°, then gradually melting and giving a clear liquid only at 77·5°. It is not changed at 100° by methyl iodide in presence or absence of methyl alcohol, but undergoes profound decomposition when boiled with a chloroform solution of bromine. With concentrated sulphuric acid it gives a yellow solution, quickly becoming violet-red with slight evolution of gas.

2:4:4-Triphenyl-1:3-oxthiophan-5-one-3-oxide,  $\text{CPh}_2 \begin{smallmatrix} \text{SO}-\text{CHPh} \\ \text{CO}\cdot\text{O} \end{smallmatrix}$ , obtained by oxidising the preceding compound, crystallises in microscopic prisms, often united in bundles, m. p. 158·5—160·5°, and in concentrated sulphuric acid yields a greenish-yellow solution becoming violet-brown when heated. When boiled with normal potassium hydroxide solution, it emits an odour of benzaldehyde.

4:4-Diphenyl-2-p-chlorophenyl-1:3-oxthiophan-5-one,



obtained from *p*-chlorobenzaldehyde, crystallises in slender, silky prisms or concentric aggregates of colourless, four-sided prisms, m. p. 125—126°, and towards concentrated sulphuric acid behaves like the chlorine-free compound.

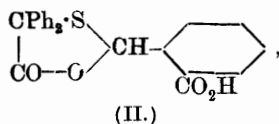
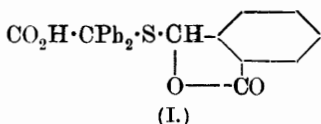
4:4-Diphenyl-2-o-nitrophenyl-1:3-oxthiophan-5-one,  $\text{C}_{21}\text{H}_{15}\text{O}_4\text{NS}$ , from *o*-nitrobenzaldehyde, forms colourless, four-sided plates, m. p. 116·5—117·5°, and gives a violet-brown solution in concentrated sulphuric acid.

4:4-Diphenyl-2-m-nitrophenyl-1:3-oxthiophan-5-one,  $\text{C}_{21}\text{H}_{15}\text{O}_4\text{NS}$ , from *m*-nitrobenzaldehyde, forms iridescent, white, quadrilateral plates, m. p. 132—133°.

4:4-Diphenyl-2-o-hydroxyphenyl-1:3-oxthiophan-5-one,  $\text{C}_{21}\text{H}_{16}\text{O}_3\text{S}$ , formed from salicylaldehyde, crystallises in colourless, microscopic rhombs, m. p. 147° (decomp.), and dissolves in concentrated sulphuric acid to a greenish-orange solution, becoming violet-brown when heated. In ammonia solution it gives a greenish-yellow solution, and in normal potassium hydroxide a greenish-brown solution which soon loses its colour. Its *acetyl* derivative,  $\text{C}_{23}\text{H}_{18}\text{O}_4\text{S}$ , forms flat prisms or concentric aggregates of microscopic, rhombic plates, m. p. 104—105°.

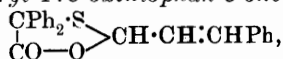
4:4-Diphenyl-2-p-anisyl-1:3-oxthiophan-5-one,  $C_{22}H_{18}O_3S$ , obtained from anisaldehyde, forms colourless, microscopic plates or heavy plates, m. p. 103—104°, and dissolves in concentrated sulphuric acid to a greenish-yellow solution, rapidly turning orange-brown.

The  $\gamma$ -lactone (I), or, possibly, (II), obtained from *o*-phthalaldehyde



hydric acid and thiobenzyllic acid, crystallises in microscopic, four-sided plates, turns blue at 150°, and decomposes at 168°; it forms also the hydrate,  $+H_2O$ , which softens at 115°. It dissolves in concentrated sulphuric acid, giving a yellowish-brown solution, quickly turning brownish-red with a violet tinge. Its barium salt was prepared and analysed.

4:4-Diphenyl-2-styryl-1:3-oxthiophan-5-one,

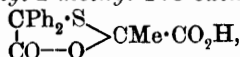


obtained from cinnamaldehyde, forms microscopic, colourless, pointed, rhombic plates, m. p. 156—157° (decomp.); its solution in concentrated sulphuric acid is orange-coloured, and slowly becomes brown or, when heated, brownish-red.

4:4-Diphenyl-2:2-dimethyl-1:3-oxthiophan-5-one,  $\begin{array}{c} \text{CPh}_2 \cdot \text{S} \\ | \\ \text{CO} \text{---} \text{O} \end{array} \begin{array}{c} \diagup \text{CMe}_2 \\ | \\ \text{O} \end{array}$ ,

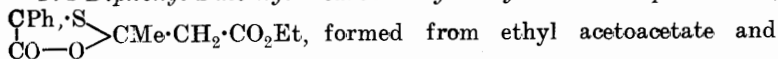
obtained from acetone and thiobenzyllic acid, forms flat, white prisms, m. p. 119.5—120.5°, gives a brownish-red solution with a violet tinge in concentrated sulphuric acid, and is decomposed into its components when boiled with alcoholic potassium hydroxide solution.

2-Carboxy-4:4-diphenyl-2-methyl-1:3-oxthiophan-5-one,



obtained from methylsuccinic acid and thiobenzyllic acid, crystallises in truncated, double pyramids or microscopic, colourless, four-sided plates, softening at 156°, m. p. 160.5—162°. Towards concentrated sulphuric acid it behaves like the preceding compound. Its silver and barium salts form amorphous, white precipitates and rapidly decompose.

4:4-Diphenyl-2-methyl-2-carbethoxymethyl-1:3-oxthiophan-5-one,



obtained from ethyl acetoacetate and thiobenzyllic acid, crystallises in drusy aggregates of colourless, four-sided prisms, m. p. 65—66.5°, and dissolves in alkali hydroxide solution and, with an orange coloration, in concentrated sulphuric acid.

Ethylxanthodiphenylacetic acid,  $\text{OEt} \cdot \text{CS} \cdot \text{S} \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$ , obtained as sodium salt by the interaction of chlorodiphenylacetic acid and

potassium xanthate in presence of sodium carbonate, forms bundles of shining, colourless prisms, sintering slightly at  $140^{\circ}$ , m. p. about  $167^{\circ}$ . Its solution in concentrated sulphuric acid is bright red with a violet tinge, and becomes turbid and orange-brown when heated. The *barium* salt was prepared and analysed. Unsuccessful attempts were made to decompose the acid with formation of thiobenzyllic acid.

Improved yields of thiobenzyllic acid may be obtained by a modification of Becker and Bistrzycki's method (A., 1915, i, 245). The product given by Bettschart and Bistrzycki's method, which involves the use of the additive compound of benzylic acid and allylthiocarbimide (A., 1919, i, 207), is less pure than that obtained with the help of phenylthiocarbimide.

Coupling of thiobenzyllic acid with acetophenone, benzophenone, dibenzyl ketone and benzil could not be effected. T. H. P.

**Syntheses in the Cinchona Series. IV. Nitro- and Amino-derivatives of the Dihydro-alkaloids.** WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1920, **42**, 1481—1489).—Using the methods described (compare D.R.-P. 283537), it was found that satisfactory results were not obtained in the preparation of 5-nitro- and 5-amino-dihydroquinine. During the nitration of dihydroquinine, sulphonation also occurred, and a nitrosulphonic acid was obtained. By nitration in fuming nitric acid (D 1.52), however, without the addition of sulphuric acid, an excellent yield of 5-nitrodihydroquinine, m. p.  $220\text{--}222^{\circ}$ ,  $[\alpha]_D^{25} - 200.0^{\circ}$  (in chloroform), was obtained. 5-Nitrodihydroquininesulphonic acid, m. p.  $260\text{--}285^{\circ}$  (decomp.),  $[\alpha]_D^{25} - 133.0^{\circ}$  (in *N*/2-sodium hydroxide), was obtained either by nitration of dihydroquininesulphonic acid or by sulphonation of 5-nitrodihydroquinine.

5-Nitrodihydroquinine is best reduced by adding it slowly, with stirring, to cold, concentrated hydrochloric acid until it is all dissolved, and then adding stannous chloride to the solution at  $0^{\circ}$ , the temperature not being allowed to rise above  $35^{\circ}$ . The base was finally obtained in yellow needles, m. p.  $220\text{--}221^{\circ}$ ,  $[\alpha]_D^{25} - 17.7^{\circ}$ .

These methods were successfully used for the preparation of nitro- and amino-derivatives from other dihydro-alkaloids of this series, the following compounds being obtained.

5-Nitroethylidihydrocupreine (5-nitro-optochin), m. p.  $225\text{--}226^{\circ}$  (decomp.),  $[\alpha]_D^{25} - 198.2^{\circ}$  (in chloroform); 5-aminoethylidihydrocupreine, m. p.  $214\text{--}215^{\circ}$  (decomp.),  $[\alpha]_D^{24.5} - 15.9^{\circ}$  (in alcohol) (compare Giemsa and Halberkann, A., 1919, i, 342).

5-Nitrodihydroquinidine, m. p.  $208\text{--}209^{\circ}$ ,  $[\alpha]_D^{25} + 326.5^{\circ}$  (in alcohol), which gives a nitrate,  $C_{20}H_{25}O_4N_3 \cdot HNO_3$ ,  $[\alpha]_D^{25} + 232.8^{\circ}$ ; 5-aminodihydroquinidine, m. p.  $235^{\circ}$ ,  $[\alpha]_D^{20} + 115.5^{\circ}$  (in alcohol).

5-Nitroethylidihydrocupreidine, m. p.  $220\text{--}221^{\circ}$  (decomp.),  $[\alpha]_D^{25} + 322.4^{\circ}$  (in alcohol); 5-aminoethylidihydrocupreidine, m. p.  $216\text{--}217^{\circ}$ ,  $[\alpha]_D^{25} - 69.4^{\circ}$  (in chloroform),  $+ 91.6^{\circ}$  (in alcohol).

5-Nitrodihydrodeoxyquinine,  $C_{20}H_{25}O_3N_3 \cdot 3\frac{1}{2}H_2O$ , m. p. 67.5—69°,  $[\alpha]_D^{25} + 80.2^\circ$  (in alcohol). Attempts to reduce this compound were not successful. W. G.

### Syntheses in the Cinchona Series. V. Dihydrodeoxyquinine and Dihydrodeoxyquinidine and their Derivatives.

MICHAEL HEIDELBERGER and WALTER A. JACOBS (*J. Amer. Chem. Soc.*, 1920, **42**, 1489—1502. Compare preceding abstract).—The series of compounds studied consisted of dihydroquinine  $\rightarrow$  chlorodihydroquinine  $\rightarrow$  dihydrodeoxyquinine  $\rightarrow$  dihydrodeoxycupreine  $\rightarrow$  ethyldihydrocupreine, and the similar series of quinidine derivatives, the methods of preparation employed being essentially those used by Koenigs (compare *Ber.*, 1895, **28**, 3147; 1896, **29**, 372) and Rabe (compare *A.*, 1910, i, 417) for the non-hydrogenated derivatives.

Dihydroquinine dihydrochloride when acted on by phosphorus pentachloride gives *chlorodihydroquinine*, m. p. 143—144°,  $[\alpha]_D^{21.5} + 42.1^\circ$  (in alcohol), giving a *hydrochloride*, m. p. 232—233° (decomp.),  $[\alpha]_D^{20.5} - 2.9^\circ$ , and on reduction *dihydrodeoxyquinine*,  $C_{20}H_{26}ON_2$ , an oil, which yields a crystalline *trihydrate*,  $[\alpha]_D^{24} - 77.5^\circ$  (in alcohol), a *picrate*, a *hydrochloride*, m. p. 179—180°,  $[\alpha]_D^{22.5} - 6.8^\circ$ , a *dihydrochloride*, and a *methiodide*,  $[\alpha]_D^{21} - 7.4^\circ$  (in alcohol). When demethylated by boiling with hydrobromic acid, dihydroquinine trihydrate yields *dihydrodeoxycupreine*, m. p. 191—191.5°,  $[\alpha]_D^{23} - 77.1^\circ$  (in alcohol), giving a *hydrochloride*, m. p. 210°,  $[\alpha]_D^{23} + 1.5^\circ$ , a *dihydrobromide*, m. p. 225—227°, a *methiodide*, m. p. 165—167°,  $[\alpha]_D^{22} - 37.6^\circ$ , and *ethyldihydrodeoxycupreine hydrochloride*, m. p. 185—186°,  $[\alpha]_D^{23} - 9.0^\circ$ . When chlorodihydroquinine is demethylated by hydrobromic acid it yields *bromodihydrocupreine dihydrobromide*, m. p. 196—197°,  $[\alpha]_D^{24} - 69.1^\circ$ .

*Chlorodihydroquinidine*, m. p. 93.5—95°,  $[\alpha]_D^{22} + 20.0^\circ$  (in alcohol), gives a *hydrochloride*, m. p. 208—209°,  $[\alpha]_D^{25} + 39.7^\circ$ , and on reduction yields *dihydrodeoxyquinidine dihydrate*, m. p. 81—83°,  $[\alpha]_D^{22.5} + 167.3^\circ$  (in alcohol), giving a *picrate*, a *hydrobromide*, m. p. 151—152°,  $[\alpha]_D^{24} + 64.5^\circ$ ; a *dihydrobromide*, m. p. 225°, and a *methiodide*, m. p. 163—164°. When demethylated, dihydrodeoxyquinidine yields *dihydrocupreidine*, m. p. 183—183.5°,  $[\alpha]_D^{24} + 183.7^\circ$ , giving a *hydrochloride*,  $[\alpha]_D^{22} + 76.8^\circ$ , a *dihydrobromide*, and a *methiodide*,  $[\alpha]_D^{23} + 95.0^\circ$ . *Bromodihydrocupreidine dihydrobromide* has  $[\alpha]_D^{24} - 47.7^\circ$ .

Chloroquinidine gives a *hydrochloride*, m. p. 199—206° (decomp.),  $[\alpha]_D^{25} + 47.7^\circ$ ; deoxyquinidine gives a *hydrochloride*, m. p. 125°,  $[\alpha]_D^{30} + 81.9^\circ$ ; quinene gives a *dihydrochloride*, m. p. 110—185°,  $[\alpha]_D^{24.5} + 18.4^\circ$ .

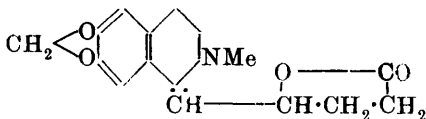
The authors suggest that in place of the prefix "deoxy" (desoxy) the suffix "ane" should be used, e.g., in place of deoxyquinine they would use quinane. W. G.

**Constitution of Lycorine [= Narcissine].** K. GORTER (*Bull. Jard. bot. Buitenzorg*, 1920, [iii], **2**, 1—7. Compare *A.*, this vol., i, 467).—Lycorine was obtained from the bulbs of *Crinum*

*giganteum* in a yield of 0.1–0.18% of the fresh material. Ewins' (narcissine) formula,  $C_{16}H_{17}O_4N$  (T., 1910, 97, 2406), was confirmed;  $[\alpha]_D^{25} - 120^\circ$ . The hydrochloride, m. p.  $206^\circ$ , is soluble in twenty parts of water at  $26^\circ$ . The mercurichloride, the picrate, and the perchlorate decompose, respectively, at  $149^\circ$ ,  $196^\circ$ , and  $230^\circ$ . Asahina and Sugii (A., 1913, i, 1093) found that lycorine when heated with phloroglucinol and sulphuric acid gives a reddish-brown precipitate, indicating the presence of a methylenedioxy-group, already surmised by Ewins. Gorter has applied this reaction quantitatively by heating lycorine on the water-bath with 30% sulphuric acid, with and without resorcinol; the difference between the weight of the two precipitates corresponds roughly with that calculated for formalresorcinol from one methylenedioxy-group.

The above facts, and the blue fluorescence produced on adding a few drops of permanganate to lycorine sulphate solution, suggested a relationship to hydrastine, further emphasised by the opposite sign of the specific rotations of the free base ( $-120^\circ$ ) and of the hydrochloride ( $+43^\circ$ ).

With hydrogen and palladous chloride, lycorine is reduced to *dihydrolycorine*,  $C_{16}H_{19}O_4N$ , prisms, m. p.  $247^\circ$ , yielding a sparingly soluble *nitrate*, m. p.  $243^\circ$ . The reduced base is not made fluorescent by permanganate, whence the author concludes that the hydroxyl of the supposed lactonic side-chain is not adjacent to the isoquinoline nucleus, as in hydrastine, but rather that the fluorescence of lycorine is due to a double



linking adjacent to this nucleus. Oxidation of lycorine with permanganate gave a small quantity of hydrastic and of oxalic acids, but no succinic acid, which leads the author to choose the annexed among various possible formulæ.

G. B.

**Ortho-para-isomerism in the Preparation of Diaminodiphenylmethane.** HAROLD KING (T., 1920, 117, 988–992).

**Manufacture of Asymmetric Carbamides.** AXEL VIGGO BLOM (Brit. Pat. 125584).—Asymmetric carbamides are produced by the action of the calculated quantity of carbonyl chloride on equimolecular proportions of an aminonaphtholsulphonic acid and a primary aromatic diamine in which the two amino-groups have different reaction speeds, in consequence of the presence of an ortho-substituent, as in the tolylenediamines, or of the substitution of one hydrogen atom by a formyl group. The operation must be conducted in such a way that the components are continuously brought into reaction in molecular proportions in a large vat, with efficient stirring, at a temperature of about  $40^\circ$  while a solution of an alkali hydroxide is run in in sufficient quantity just to neutralise the hydrogen chloride liberated.

G. F. M.



**Preparation of Derivatives of *p*-Nitrophenylcarbamide.**

FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 319970; from *Chem. Zentr.*, 1920, iv, 132—133).—*p*-Nitrophenylcarbamide chloride is caused to react with primary or secondary bases or their substitution products, particularly sulphonic acids, hydroxy-sulphonic acid, etc., with or without reagents which absorb hydrogen chloride. The greenish-yellow lake-dye, *pp'*-*dinitrodiphenylcarbamide*, is obtained by heating *p*-nitrophenylcarbamide chloride with *p*-nitroaniline and nitrobenzene, or by the direct action of carbonyl chloride (1 mol.) on *p*-nitroaniline (2 mols.) if the initial temperature is not too high. Sodium sulphanilate and *p*-nitrophenylcarbamide chloride react in the presence of water and sodium acetate to yield sodium *pp'*-*nitrodiphenylcarbamidesulphonate*, yellow, crystalline powder, sparingly soluble in water, which is reduced by sodium sulphide solution to the corresponding colourless, more readily soluble *amino*-compound. The dark yellow sodium *ethylenebis-pp'*-*nitrodiphenylcarbamidesulphonate* is prepared from sodium *pp'*-diaminostilbenesulphonate. H. W.

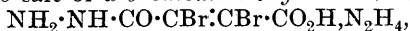
**Degradation Experiments with Dibromomaleic and Chlorofumaric Acids.**

PAUL RUGGLI and CARL HARTMANN (*Helv. Chim. Acta*, 1920, 3, 493—514).—The authors have subjected dibromomaleic acid to those reactions which, as a rule, convert an acid into an amine with one carbon atom less than the acid, the object being to obtain the brominated amine,  $\text{NH}_2\cdot\text{CBr}\cdot\text{CBr}\cdot\text{NH}_2$ .

Ethyl dibromomaleate (compare Michael, A., 1893, i, 144; Pum, A., 1888, 1058; Ruhemann and Cunningham, T., 1899, 75, 962) may be prepared by heating an alcoholic solution of dibromomaleic anhydride and hydrogen chloride under pressure. Attempts to obtain ditertiary glycols, and hence, by loss of water, dihydrofuran derivatives, by treating ethyl dibromomaleate with organomagnesium compounds, yielded unsatisfactory results. Ethyl hydrogen dibromomaleate,  $\text{CO}_2\text{H}\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CO}_2\text{Et}$ , crystallises in pale yellow, radiating needles, m. p. 65—67°; Salmony and Simonis gave m. p. 100°, which is erroneous (A., 1905, i, 631).

*Dibromomaleic diamide*,  $\text{NH}_2\cdot\text{CO}\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CO}\cdot\text{NH}_2$ , forms slender, colourless needles, turns brown at 120°, and decomposes with evolution of bromine at 200°. Treatment of the diamide with bromine in a sealed tube at 90° yields dibromomaleimide, m. p. 227° (compare Dunlap, A., 1896, i, 471).

The *hydrazine* salt of *dibromomaleichydrazidic acid*,

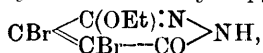


forms slender, white needles, m. p. about 130° (decomp.), and in aqueous solution reacts with ammoniacal silver solution in the cold, whilst with neutral silver nitrate, silver dibromomaleate is precipitated. By dilute sulphuric acid, hydrazine sulphate is precipitated, and the action of benzaldehyde precipitates both the hydrazine molecules as benzylideneazine. By prolonged boiling

with dibromomaleic anhydride in alcoholic solution, the salt is converted quantitatively into the ammonium salt of

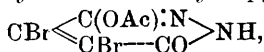
*Dibromomaleic hydrazide* [4:5-dibromo-3:6-diketo-1:2:3:6-tetrahydropyridazine],  $\text{CBr} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CBr} \cdot \text{CO} \end{smallmatrix} \text{NH}$ , which forms yellow needles and is a highly stable compound; when slowly heated to above  $300^\circ$ , it gradually turns brown and decomposes, and when immersed in a bath at  $340^\circ$  it melts and decomposes. The *ammonium* salt,  $\text{C}_4\text{H}_2\text{O}_2\text{N}_2\text{Br}_2 \cdot \text{NH}_3$ , forms almost colourless crystals, and does not reduce ammoniacal silver solution. The two *silver* salts,  $\text{C}_4\text{HO}_2\text{N}_2\text{Br}_2\text{Ag}$  and  $\text{C}_4\text{O}_2\text{N}_2\text{Br}_2\text{Ag}_2$ , the *barium* salt (+  $6\text{H}_2\text{O}$ ), and other salts have been prepared.

4:5-Dibromo-3-ethoxy-6-keto-1:6-dihydropyridazine,



obtained by heating the di-silver salt of the preceding compound with ethyl iodide and alcohol, crystallises in white leaflets, m. p.  $206^\circ$ ; its *silver* salt was prepared, but not in a pure state.

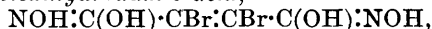
4:5-Dibromo-3-acetoxy-6-keto-1:6-dihydropyridazine,



forms crystals, sintering at  $225^\circ$ , m. p.  $228^\circ$ , and has the normal molecular weight in boiling alcohol.

*Ethylenediamine dibromomaleate*,  $\text{C}_4\text{H}_2\text{O}_4\text{Br}_2 \cdot \text{C}_2\text{H}_8\text{N}_2$ , forms slender, white needles, turning brown at about  $170^\circ$ , and then decomposing.

*Dibromomaleicdihydroxamic acid*,



forms a hygroscopic, non-crystallisable mass; the *sodium* salt,  $\text{C}_4\text{H}_2\text{O}_4\text{N}_2\text{Br}_2\text{Na}_2$ , is also hygroscopic.

Chlorofumaric chloride,  $\text{COCl} \cdot \text{CCl} \cdot \text{CH} \cdot \text{COCl}$ , prepared from tartaric acid and phosphorus pentachloride (compare Perkin, T., 1888, **53**, 696), may be freed from chlorides of phosphorus by shaking with water, if care be taken that no heating occurs. The diethyl ester of chlorofumaric acid, prepared by dropping alcohol on to the crude chloride (compare Claus, A., 1878, 855), gives vapour which strongly attacks the eyes.

*Ethyl pyrazolone-3-carboxylate*,  $\begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ \text{NH} - \text{N} \end{smallmatrix} \gg \text{C} \cdot \text{CO}_2\text{Et}$  (compare

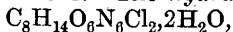
Rothenburg, A., 1893, i, 180, 367, 730; Ruhemann, T., 1896, **69**, 1394), prepared by the interaction of ethyl chlorofumarate and hydrazine hydrate, forms crystals, m. p.  $178^\circ$ , and with fuming nitric acid yields a violet solution giving, on neutralisation, a violet compound, m. p.  $164^\circ$ .

*Bismonochlorofumarylhydrazine*,



obtained as hydrazine salt by the interaction of chlorofumaric chloride and hydrazine hydrate, forms almost colourless crystals, m. p. above  $360^\circ$ , and reduces ammoniacal silver solution in the

hot, but not Fehling's solution; it dissolves only in alkali solutions, giving deep yellow colorations. The *hydrazine* salt,



forms somewhat unstable, deep yellow crystals, m. p.  $218^\circ$ , and reduces Fehling's solution and ammoniacal silver solution immediately.

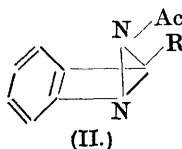
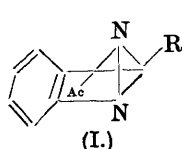
T. H. P.

### Structure- and Stereo-isomerism of Indazole Derivatives and the Constitution of Indazole.

KARL VON AUWERS and MARIANNE DÜESBERG (*Ber.*, 1920, **53**, [B], 1179—1210).—Further details of the preparation and properties of the 1- and 2-alkyl-indazoles are recorded (compare A., 1919, i, 455), and the corresponding quaternary salts have been fully investigated. It is shown that the 2-alkyl derivatives, like the 1-alkyl compounds, have the power of uniting with one molecular proportion of alkali iodide, but that a second proportion cannot be added, although the quaternary iodide still contains a tertiary nitrogen atom. Identical products are obtained by the action of the isomeric 1- and 2-alkyl-indazoles on the iodide of the same alkyl, but isomeric quaternary compounds result from the interaction of alkylindazoles with the iodide of a different alkyl radicle. Homologous alkylindazoles of the same series give different additive products with reciprocal homologous alkyl iodides, whilst homologous alkylindazoles of different series give identical results when similarly treated. The quaternary iodides liberate alkyl iodide when heated above their melting points. The 1-alkyl derivatives eliminate the added alkyl iodide, and thus re-form the parent substance; on the other hand, the 2-alkyl compounds lose the alkyl group of the base in the form of alkyl iodide, and retain the radicle of the iodide used, or, in other words, the product of fission is a 1-alkyl derivative. The observations are most readily explained by assuming the general structure  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \\ \text{NR}' \end{smallmatrix} \text{N} \begin{smallmatrix} \text{R} \\ \text{I} \end{smallmatrix}$ , for the quaternary iodides. A

method of converting 2-alkylindazoles into 1-derivatives is thus given, and also the simplest and best method of preparing the latter in the pure state.

Further instances of stereoisomerism among acylindazoles are recorded, and more definite evidence is adduced that the observed phenomena are actually due to stereoisomerism. The capability to

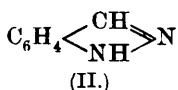
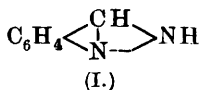


yield such stereoisomerides disappears when an alkyl group is introduced into the 3-position. Apparently the possibility of stereoisomerism depends on the presence of a tervalent nitrogen atom in the ring, as

indicated by the annexed formulæ, and the phenomena are thus similar to those recently observed by Freund and Kessler and by Hess. The apparent disappearance of stereoisomerism in the cases of the alkyl derivatives finds its parallel in the frequent formation

of stereoisomeric aldoximes and the infrequent occurrence of isomerides of the type of acetophenoneoxime.

The authors have attempted to bring all available chemical and physical evidence to bear on the problem of the elucidation of the constitution of indazole itself. They are led to the conclusion that this cannot at present be conclusively settled, but that the balance of the evidence is greatly in favour of formula I rather than II.



2-Methylindazole, prisms or plates, m. p.  $56^\circ$ , b. p.  $261^\circ$ /ordinary pressure,  $135^\circ/16$  mm., is prepared from methyl iodide and indazole, from silver indazole and methyl iodide, and from 2-methylindazole-3-carboxylic acid at  $230^\circ$ ; when crystallised from water, it appears to form a monohydrate (compare Schad, A., 1893, i, 280). It forms crystalline double compounds with silver nitrate and mercuric chloride. The *picrate* forms yellow, silky needles, m. p.  $168^\circ$ . 1-Methylindazole, m. p.  $60\text{--}61^\circ$ , b. p.  $231^\circ$ /ordinary pressure,  $109^\circ/17$  mm., is prepared from 1-methylindazole-3-carboxylic acid, or by the alkylation of indazole with methyl iodide and sodium methoxide; the mixture of the 1- and 2-methyl derivatives obtained by the latter method is separable by fractional distillation under ordinary or diminished pressure, or by crystallisation of the *picrates*. 1-Methylindazole *picrate* forms slender, yellow needles or coarse, transparent crystals, m. p.  $136\text{--}137^\circ$ . 1-Methylindazole yields crystalline double compounds with mercuric chloride and silver nitrate. 1:2-Dimethylindazolium iodide, m. p.  $187^\circ$ , is prepared by heating either 1- or 2-methylindazole with an excess of methyl iodide at  $100^\circ$ ; the corresponding *picrate* has m. p.  $167\text{--}168^\circ$ . 2-Ethylindazole is a pale yellow oil, b. p.  $268^\circ$ /ordinary pressure,  $140^\circ/14$  mm.; the *picrate*, m. p.  $155\text{--}156^\circ$ , is immediately precipitated from dilute ethereal solution in the form of slender needles, which are gradually transformed into coarse, transparent crystals. 1-Ethylindazole is a colourless oil, b. p.  $126\text{--}127^\circ/21$  mm. (*picrate*, thin, pale yellow needles, m. p.  $148\text{--}150^\circ$ ). The action of ethyl iodide on 1-methylindazole or of methyl iodide on 2-ethylindazole at  $100^\circ$  leads to the production of 1-methyl-2-ethylindazolium iodide, small, colourless needles, m. p.  $172\cdot5\text{--}173^\circ$  (*picrate*, m. p.  $196\text{--}197^\circ$ ). 2-Methyl-1-ethylindazolium iodide, m. p.  $154^\circ$ , is similarly prepared from 2-methylindazole and ethyl iodide or 1-ethylindazole and methyl iodide; the corresponding *picrate* has m. p.  $149\text{--}150^\circ$ . 1:2-Diethylindazolium iodide forms coarse, colourless crystals, m. p.  $134^\circ$  (*picrate*, m. p.  $153^\circ$ ). 2:3-Dimethylindazole, m. p.  $79\text{--}80^\circ$ , yields a *picrate*, m. p.  $224\text{--}225^\circ$ , and is converted by methyl iodide into 1:2:3-trimethylindazolium iodide, colourless, silky needles, m. p.  $220\text{--}221^\circ$ . Decomposition by heat proceeds normally in the cases of 1:2-dimethylindazolium iodide, 2-methyl-1-ethylindazolium iodide, and 1:2:3-trimethylindazolium iodide,

the product in the latter case being the 1:3-dimethyl derivative. 1-Methyl-2-ethylindazolium iodide yielded a mixture of 1-methylindazole (at least 75%) and 2-ethylindazole.

The stable form of 2-acetylindazole yields a crystalline *hydrochloride*, which is decomposed by exposure to moist air. The labile variety is completely transformed into the stable isomeride when heated for thirty minutes at 100°. The additive compound of the labile form and mercuric chloride has m. p. 174—175°. Hydrogen chloride decomposes the labile variety, with formation of indazole hydrochloride. Stable 2-*propionylindazole*, from indazole and propionic anhydride at the ordinary temperature, has b. p. 267°, m. p. 52°; it appears to be dimorphous. The labile *propionate* (from the silver salt or by the pyridine method) forms pearly leaflets or shining, rhombic plates, m. p. 100·5—101·5°; it has b. p. 267°, and is then quantitatively converted into the stable variety. The stable *benzoate* crystallises in slender, colourless needles, m. p. 94—95°. The labile *isomeride* forms small, coarse, colourless crystals, m. p. 78°; it can be distilled without decomposition at the ordinary pressure, and is thereby converted into the stable variety; the same change occurs slowly at the ordinary temperature, rapidly at 100°. Attempts to acetylate 3-methylindazole by methods similar to those outlined above in connexion with the propionyl derivative led only to the formation of 2-acetyl-3-methylindazole, m. p. 72—73°. Similarly, only one form of 2-acetyl-3-ethylindazole, slender prisms or large, well-defined crystals, m. p. 35·5—36·5°, could be prepared from 3-ethylindazole.

*o*-Nitrobenzoyl chloride is conveniently prepared by the action of thionyl chloride on *o*-nitrobenzoic acid, and is converted by ethyl methylacetoacetate and sodium into *ethyl o-nitrobenzoylmethylacetoacetate*, which is hydrolysed by sulphuric acid (1:1) to *o-nitropropiofenone*, pale yellow, viscous, odourless oil, b. p. 166—167°/15 mm., 161°/10—11 mm. (*semicarbazone*, m. p. 182—183°); it is reduced by a large excess of stannous chloride to *o-aminopropiofenone*, pale yellow leaflets or hexagonal platelets, m. p. 46—47° (*oxime*, needles, m. p. 88—89°). The aminoketone is converted according to the method of Fischer and Tafel into 3-ethylindazole, slender, interwoven needles or coarse prisms, m. p. 74·5—75·5°, b. p. 290°/atmospheric pressure, 157—158°/15 mm. The *picrate* has m. p. 152·5—153·5°. 2:3-Diethylindazole, from 3-ethylindazole and ethyl iodide at 200°, is a colourless oil, b. p. about 287—290°, which does not show any tendency to crystallise; the *picrate* forms pale yellow needles, m. p. 184—186° after previous softening. H. W.

### Stereoisomeric Acyl Derivatives of Substituted Indazoles.

K. VON AUWERS and K. SCHWEGLER (*Ber.*, 1920, **53**, [B], 1211—1232).—It has been shown previously (preceding abstract) that 2-acyl derivatives of indazole exist in two stereoisomeric forms of differing stability, whilst similar instances of stereo-

isomerism have not up to the present been observed with derivatives of the 3-alkylindazoles. The present communication deals with the effect of the entrance of substituents in the benzene nucleus. In every case which has been investigated, it has been found possible to isolate stereoisomeric acyl derivatives. The stability of the labile isomerides varies very greatly; in some instances the substances cannot be preserved unchanged for more than a few minutes, even at the ordinary temperature, whilst in others they can be heated for hours on the water-bath, and even maintained in the molten condition for a short time without undergoing transformation. The benzoyl derivatives are more stable than the corresponding acetyl compounds. In general, for some unexplained reason, the chemical nature of the substituent appears to have less influence on the stability of the derivative than has its position in the benzene nucleus. At present it is not possible to establish any definite connexion between the melting points and relative stabilities of the isomerides.

The stable acetyl and benzoyl derivatives are prepared by the action of warm acetic or benzoic anhydride on the indazoles. The labile compounds are obtained by the action of the requisite acid chloride on a suspension of the silver salt of the indazole in absolute ether; a few labile acetyl derivatives were prepared by the pyridine method. The following individual substances are described: 6-nitroindazole, m. p.  $181^{\circ}$  (2-acetyl derivative, stable form, m. p.  $140-141^{\circ}$ , labile form, colourless leaflets, m. p.  $74-75^{\circ}$ ; 2-benzoyl derivative, stable form, m. p.  $164-165^{\circ}$ , labile form, yellowish-white, silky needles, m. p.  $133-134^{\circ}$  or  $140^{\circ}$  for different preparations). 6-Nitroindazole does not behave as definitely as indazole itself and its methyl derivatives towards methylating agents under varying conditions; thus, when heated with an excess of methyl iodide at  $100^{\circ}$ , it gives mainly 6-nitro-2-methylindazole, m. p.  $159-160^{\circ}$ , mixed, however, with 6-nitro-1-methylindazole, yellow, matted needles, m. p.  $108-109^{\circ}$ . When alkylation is effected in the presence of sodium methoxide, a mixture of the 1- and 2-methyl derivatives is likewise produced, the former being in excess. The constitution of 6-nitro-2-methylindazole is deduced by its reduction to 6-amino-2-methylindazole, long, intertwined needles, m. p.  $156-157^{\circ}$ , which, after diazotisation and elimination of the diazo-complex, yields 2-methylindazole. 5-Nitroindazole, m. p.  $208^{\circ}$ , gives a stable acetyl derivative, m. p.  $158-159^{\circ}$ , and a labile compound, long, slender silky needles, m. p.  $138-139^{\circ}$ ; the corresponding stable benzoyl derivative crystallises in pearly leaflets, m. p.  $193-194^{\circ}$ , whilst the labile substance forms prisms, m. p.  $155^{\circ}$ , when plunged into a bath pre-heated to  $150^{\circ}$ , but otherwise depending on the rate of heating. 4-Nitroindazole, m. p.  $202-203^{\circ}$ , is converted into stable and labile acetyl derivatives, colourless, silky needles, m. p.  $144.5-145.5^{\circ}$ , and small, pale yellow needles, m. p.  $119-121^{\circ}$ , respectively; the stable benzoyl compound has m. p.  $162-163^{\circ}$ , whilst the labile form, pale yellow, slender needles, has m. p.  $130-132^{\circ}$ . 4-Nitroindazole is reduced

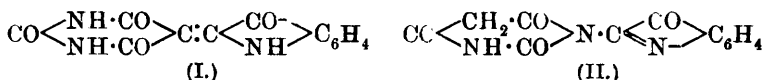
by ferrous sulphate and excess of ammonia to 4-aminoindazole, colourless, shining leaflets, m. p. 150—151·5° (the *hydrochloride*, *nitrate*, *sulphate*, and *picrate*, greenish-yellow needles, which decompose without melting at 175—180° after darkening at 170°, are also described). 2-Acetyl-4-acetylaminindazole is prepared in a stable modification, colourless, shining leaflets, m. p. 201—202·5°, and a labile form, pale yellow crystals, m. p. 155—160°. When either variety is warmed with dilute hydrochloric acid, 4-acetylaminindazole hydrochloride is obtained in long needles, m. p. 223—225°, from which the free base, coarse prisms, m. p. 145—148°, is isolated in the usual manner. 4-Cyanindazole forms yellow, flat needles, m. p. 157—160°. 7-Nitroindazole, m. p. 186·5—187·5°, yields a very readily hydrolysed, stable acetate, m. p. 132·5—134°; the corresponding labile variety could not be isolated with certainty, apparently owing to its extraordinary ease of hydrolysis.

5-Chloro-*o*-toluidine, b. p. 118—120°/18 mm., is converted into its *benzoyl* derivative, colourless needles, m. p. 165—166°, which is transformed through the *nitroso*-derivative into 5-chloroindazole, slender, shining needles, m. p. 119—120° (*picrate*, m. p. 193—195°); its stable and labile *acetates* have m. p.'s 144—145° and 119—120° respectively.

5-Methylindazole, m. p. 117°, is conveniently obtained from benzo-*m*-4-xylydide, which is converted into its unstable *nitroso*-compound, m. p. about 71—74°, which, when preserved in benzene solution, passes into the desired compound (*picrate*, thin, pale yellow needles or darker yellow needles grouped in rosettes, m. p. 169—170°). The stable *acetate* forms shining leaflets or flat needles, m. p. 49°, whilst the *labile* variety crystallises in colourless, transparent leaflets, m. p. 110—111°. The stable and labile *propionyl* compounds have m. p.'s 59—60° and 97—98° respectively, whilst the m. p.'s of the corresponding *benzoyl* derivatives are 89·5—90·5° and 120—121°. Treatment of 5-methylindazole with an excess of methyl iodide at 100° yields 2:5-dimethylindazole, coarse prisms, m. p. 76—77°, b. p. 270°/atmospheric pressure (the *picrate*, yellow, silky needles, m. p. 197—198°, mercuric chloride double salt, small, colourless prisms, m. p. about 220°, and silver nitrate additive compound, small, slender needles, m. p. 124·5—125·5°, are described). Alkylation with methyl iodide and sodium methoxide, on the other hand, appears to lead almost exclusively to the production of 1:5-dimethylindazole, colourless needles, m. p. 62—63° (*picrate*, m. p. 159—160°, mercuric chloride and silver nitrate additive compounds, m. p.'s 172—173° and 157—158° respectively). 6-Methylindazole, shining leaflets, m. p. 177—178° (*picrate*, m. p. 163·5—164·5°), forms an oily, stable *acetyl* compound, b. p. 146—147°/16 mm., and a labile *derivative*, colourless, shining leaflets, m. p. 116—118°. H. W.

**A New Indigoid Dyestuff.** 5-(Dioxy-2:4-pyrimidine)-2-indoleindigo [5(2')-Indoxylpyrimidine-2:4:6-trione]. J. MARTINET and O. DORNIER (*Compt. rend.*, 1920, 171, 184—187).

When some of the technical fusion of indoxyl is added to an acetic acid solution of alloxan heated on a water-bath, 5(2')-indoxylpyrimidine-2:4:6-trione is obtained in opaque, violet needles. It dyes wool and silk heliotrope, and even has a certain affinity for cotton. Its sulphonic derivative dyes wool and silk violet. To this compound the authors assign the constitution I, although this



constitution has already been assigned by Felix and Friedländer (compare A., 1910, i, 278) to a compound prepared by them from barbituric acid and isatin anilide. They contrast the properties of these two compounds, and consider that the constitution of the latter compound is better represented by formula II. W. G.

**Fission of Organic Dyes by Hydrogenation.** RICHARD MEYER (*Ber.*, 1920, 53, [B], 1265—1276).—Alizarin direct violet R and alizarin direct green G of the Höchst Farbwerke are decomposed by hydriodic acid with the formation of leucoquinizarin and *p*-toluidine-2-sulphonic acid, and are thus isomeric with alizarin irisol and alizarin cyanine green G of the Farbenfabriken Friedr. Bayer & Co., which, when similarly treated, give leucoquinizarin and *p*-toluidine-3-sulphonic acid. It is remarkable that whilst *p*-toluidine-2-sulphonic acid condenses readily with quinizarin or leucoquinizarin, *p*-toluidine-3-sulphonic acid is unable to undergo such condensation, possibly because of internal salt formation between the neighbouring amino- and sulphonic groups.

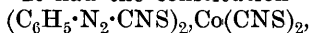
The utility of concentrated hydriodic acid in effecting the fission of azo-dyes has been examined in a number of instances and its efficiency compared with that of sodium hyposulphite. In general, an aqueous or alcoholic solution of the dye is heated with an excess of concentrated hydriodic acid until action appears to be complete; the liberated iodine is removed by sulphurous acid and the hydriodic acid by evaporation with concentrated hydrochloric acid. The method has the great advantage over other reduction processes that it does not introduce any inorganic salts into the solution. Methyl-orange is decomposed by sodium hyposulphite or by hydriodic acid into *p*-aminodimethylaniline (acetyl derivative, m. p. 130°) and sulphanilic acid, whilst diphenylamine-orange gives *p*-aminodiphenylamine, m. p. 66°, and sulphanilic acid. Metanilic acid and *p*-aminodiphenylamine are obtained from metanil-yellow, whilst Congo-red yields benzidine and 1:2-naphthylenediamine-4-sulphonic acid. Naphthylene-red gives 1:5-naphthylenediamine and 1:2-naphthylenediamine-4-sulphonic acid. H. W.

**New Catalytic Elements for the Transformation of Diazotised Compounds.** A. KORCZYŃSKI, W. MROZIŃSKI, and W. VIELAU (*Compt. rend.*, 1920, 171, 182—184).—In certain of the changes brought about in the Sandmeyer reactions it is found



that the copper salt may quite well be replaced by the corresponding nickel or cobalt salt. Thus the double cyanide of nickel and potassium may replace that of copper and potassium for the preparation of nitriles from the corresponding diazonium salts. Cobalt is not satisfactory for this change.

Cobalt thiocyanate is an excellent catalyst for the conversion of diazonium salts into the corresponding thiocyanate, and in this case the intermediate double *compound* could be isolated from benzene-diazonium chloride. It had the constitution



and was obtained as a malachite-green, crystalline powder.

The preparation of chloro- or bromo-benzene from benzene-diazonium chloride or bromide by the nickel or cobalt haloids only resulted in very poor yields, and took place only in boiling solution.

Zinc and iron salts showed no sign of any catalytic action for these changes.

W. G.

**Preparation of Methyl Red.** LOUIS DESVERGNES (*Ann. Chim. anal.*, 1920, [ii], 2, 209—210).—A solution of 89 grams of sodium nitrite in 150 c.c. of water is added slowly, with stirring, to a mixture of 137 grams of anthranilic acid, 1000 grams of water, 222 c.c. of hydrochloric acid (22°), and 300 grams of powdered ice. During the addition the temperature must not rise above 5°. After twenty minutes the mixture is added to 121 grams of dimethylaniline dissolved in 90 c.c. of hydrochloric acid (22°) and 200 c.c. of water, and, when the mixture has been stirred for a few minutes, 165 grams of sodium acetate dissolved in 500 c.c. of water are introduced. The purple-red crystals which form (in a few hours) are collected, washed with cold water, dried at 50°, and recrystallised from alcohol.

W. P. S.

**The Classification of the Proteins.** PIERRE THOMAS (*Bull. Soc. chim. Biol.*, 1920, 2, 112—118).—The existing classifications are reviewed, and the desirability of adhering to a simple and uniform international scheme is emphasised.

J. C. D.

**Barger's Microscopical Method of Determining Molecular Weights. II. Its Application to Caseinogen.** KUMAO YAMAKAMI (*Biochem. J.*, 1920, 14, 522—533).—The author confirms the observation of Robertson ("The Physical Chemistry of Proteins," 1918) that the molecular and ionic concentration of alkali caseinogenate solutions of neutral and alkaline reaction is conditioned by the concentration of the alkali solution in which the caseinogen is dissolved. The osmotic concentration of alkali caseinogenate solutions of acid reaction is dependent on the amount of dissolved caseinogen, and the mean weight of the ions in solution is about 2000.

The solubility of caseinogen in alkali solutions containing a certain amount of alkali chloride is almost twice that of caseinogen in pure alkali solution. This probably offers an explanation of the high solubility figures obtained by Robertson (*loc. cit.*) and Van Slyke

and Bosworth (A., 1913, i, 660). The true solubility of caseinogen in pure alkali must be  $22.5-25 \times 10^{-5}$  gram-equivalent alkali per gram caseinogen, and the molecular weight of alkali caseinogenate which is soluble in distilled water must be 4000—4400. W. G.

**The Influence of Salts on the Optimum Condition of Precipitation of Caseinogen.** L. MICHAELIS and ALBERT V. SZENT-GYÖRGYI (*Biochem. Zeitsch.*, 1920, **103**, 178—185).—The change in the optimum condition of precipitation of caseinogen by acetic acid and sodium acetate in the presence of salts is brought about by the action of the anion and the cation of the salts. When the action of the cation is stronger, the optimum flocculation is shifted to the less acid zone and vice versa. When the activity of both ions is the same no change in the optimum takes place. A table and curves of the results obtained with various salts are given. S. S. Z.

**The Mode of Action of Chlorine on Oxyhæmoglobin.** ANDRÉ MAYER and FRED VLÈS (*Bull. Soc. chim. Biol.*, 1920, **2**, 96—111).—A series of products are formed, which are characterised by their spectra, during the action of chlorine on hæmoglobin. It is probable that following the inhalation of large doses of chlorine the same series of reactions occurs as may be obtained in vitro. J. C. D.

**Hæmocyanin. IV. Visible Absorption Spectrum of Oxyhæmocyanin.** C. DHÈRE and A. BURDEL (*J. Physiol. Path. gen.*, 1920, **18**, 685—701).—The results of these spectrographic studies show that the oxyhæmocyanins of the gastropod molluscs of the cephalopods and of both the marine and fresh-water crustaceans give a clear and intense absorption band in the yellow when examined in suitable concentrations and solvents. The solutions examined were sufficiently clear and yet rich enough in pigment to give the characteristic band when intense illumination was employed. The solutions of oxyhæmocyanin do not contain tetronerythrin in appreciable quantities. Slight variations in the axis of absorption are considered as due to differences in the amounts of electrolytes present in the solutions examined. Photographs are appended. CHEMICAL ABSTRACTS.

**Acidity of Ash-free and of Commercial Gelatin Solutions.** H. E. PATTEN and T. O. KELLEMS (*J. Biol. Chem.*, 1920, **42**, 363—366).—The isoelectric point of ash-free gelatin lies at  $p_H=4.8$ , corresponding with a hydrogen-ion concentration of  $1.59 \times 10^{-5}$ , and that of commercial gelatin at  $p_H=5.64$ , with hydrogen-ion concentration  $2.28 \times 10^{-5}$ . The displacement of the isoelectric point of commercial gelatin is due to its alkali content. W. G.

**Effect of Salts of Heavy Metals on a Protein and the Reversal of such Effects.** ROBERT A. KEHOE (*J. Lab. Clin. Med.*, 1920, **5**, 443—452).—The coagulation of gelatin, under the

influence of salts of heavy metals, is not an irreversible reaction, but may be reversed through the action of alkalis or the neutral salts of the alkali and alkaline-earth metals. Not all such salts are of the same value in producing this effect, there being a marked secondary dependence on the acid radicle combined with the metal. Thiocyanates and iodides are more effective than bromides and chlorides. Reversal occurs most readily if the alkali or salt is added soon after the coagulation of gelatin by the heavy metal has been caused, and if heat is used. Coagulation of gelatin by heavy metals may be completely inhibited by the previous or simultaneous addition of alkalis or salts of the alkali or alkaline earth metals in sufficiently high concentrations, even when these are not of such nature as to combine with the coagulant. It is suggested that the metals react with the gelatin to form definite compounds as do the same metals with the fatty acids to form soaps. On the basis that the poisonous effects of the heavy metals on the body are due to coagulation of body proteins, the author believes that the administration of alkalis and salts of the alkali and alkaline-earth metals would be of benefit in lead and mercury poisoning, by reversing the coagulation of the proteins.

CHEMICAL ABSTRACTS.

**Relation between the Internal Complex Metallic Salts and the Solubility of Silk in Ammoniacal Nickel Solutions. The Biuret Reaction (Cu, Ni, Co) of Silk and Wool.** M. BATTEGAY and THÉODORE VOLTZ (*Bull. Soc. chim.*, 1920, [iv], 27, 536—540).—The colour changes and ultimate solution of silk when it is immersed in an ammoniacal solution of a nickel salt are explained as due to the formation of a complex nickel salt with a cyclic structure. The changes occurring are considered to be similar to those of the biuret reaction, and it is shown that under suitable conditions similar colour reactions may be obtained with silk and alkaline solutions of copper and cobalt salts.

When wool is dissolved in warm aqueous sodium hydroxide and to the solution an excess of copper sulphate is added, a rose-coloured liquid is obtained after filtration. Nickel salts give similar phenomena. Similar results are also obtained if the wool is first partly hydrolysed by acid and then treated with alkali and copper sulphate.

W. G.

**Does Chloropicrin Act on the Soluble Ferments ?** GABRIEL BERTRAND and (MME) ROSENBLATT (*Compt. rend.*, 1920, 171, 137—139).—Chloropicrin was found to possess only a very slight inhibiting influence on the action of the various soluble ferments, sucrase, amygdalinas, urease, catalase, zymase, laccase, and tyrosinase, which were examined.

W. G.

**Silicon as a Substitute for Carbon in Organic Compounds.** ARTUR BYGÉN (*Diss., Upsala*, 1916, pp. 189).—A historical summary of the chemistry of silicon compounds and their relation to the corresponding carbon compounds is given, followed by a study of the physical relations between the two classes of substances.

Mono-derivatives,  $\text{RSiCl}_3$ , are easily obtained in most cases, disubstituted derivatives are very difficult to prepare, whilst tetrasubstituted derivatives are the most easily obtained because an excess of the Grignard reagent can be used.

The b. p.'s under diminished pressure and the densities at different temperatures of the following compounds are recorded:  $\text{RSiCl}_3$ , where  $\text{R} = \text{Et}$ ,  $\text{Pr}$ , butyl, *isobutyl*, *isoamyl*,  $\text{Ph}$ , and  $\text{CH}_2\text{Ph}$ ;  $\text{R}_2\text{SiCl}_2$ , where  $\text{R} = \text{Et}$  and  $\text{Pr}$ ;  $\text{RSiEtCl}_2$ , where  $\text{R} = \text{Pr}$ , *isobutyl*, and  $\text{Ph}$ ;  $\text{SiR}_4$ , where  $\text{R} = \text{Me}$  and  $\text{Et}$ ;  $\text{SiR}_3\text{R}'$ , where  $\text{R} = \text{Me}$  or  $\text{Et}$  and  $\text{R}' = \text{Et}$ ,  $\text{Pr}$ , butyl, *isobutyl*, *isoamyl*,  $\text{Ph}$ , and  $\text{CH}_2\text{Ph}$ ;  $\text{SiMe}_2\text{R}_2$ , where  $\text{R} = \text{Et}$  and  $\text{Pr}$ ;  $\text{SiMeEtR}_2$ , where  $\text{R} = \text{Pr}$ , *isobutyl*, and  $\text{Ph}$ ;

$\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{SiR}_2$ , where  $\text{R} = \text{Cl}$  and  $\text{Me}$ .

*Benzyltrimethylmethanesulphonic acid*, rectangular tablets with  $2\text{H}_2\text{O}$ , m. p. (anhydrous)  $142\cdot2$ — $144\cdot2^\circ$ , obtained by shaking the hydrocarbon with fuming sulphuric acid (6%  $\text{SO}_3$ ), forms the salts *ammonium*, *potassium* ( $1\text{H}_2\text{O}$ ), *sodium* ( $2\text{H}_2\text{O}$ ), *lithium* ( $1\text{H}_2\text{O}$ ), *calcium* ( $0\cdot5\text{H}_2\text{O}$ ), *strontium* ( $2\text{H}_2\text{O}$ ), *barium* ( $3\text{H}_2\text{O}$ ), *magnesium* ( $7\text{H}_2\text{O}$ ), *zinc* ( $6\text{H}_2\text{O}$ ), *cadmium* ( $3\text{H}_2\text{O}$ ), *ferrous* ( $7\text{H}_2\text{O}$ ), *nickel* ( $8\text{H}_2\text{O}$ ), *cobalt* ( $8[?] \text{H}_2\text{O}$ ), *lead* ( $2\text{H}_2\text{O}$ ), *copper* ( $6\text{H}_2\text{O}$ ), and *silver* ( $1\text{H}_2\text{O}$ ). The acid *chloride*, tablets or prisms, m. p.  $58\cdot7$ — $59\cdot2^\circ$ , acid *bromide*, m. p.  $65\cdot5$ — $66^\circ$ , *amide*, needles or scales, m. p.  $101^\circ$ , *methylamide*, m. p.  $94\cdot8$ — $95\cdot3^\circ$ , *anilide*, m. p.  $137^\circ$ , *methylanilide*, m. p.  $97\cdot8$ — $98^\circ$ , *o-toluidide*, leaflets, m. p.  $156$ — $157^\circ$ , *p-toluidide*, m. p.  $117$ — $118\cdot2^\circ$ , and *benzylamide*, m. p.  $141\cdot5$ — $141\cdot7^\circ$ , are described. By fusion with potassium hydroxide the potassium salt is converted into  $\beta\beta\beta$ -trimethylethylphenol,  $\text{CMe}_3 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , needles, m. p.  $118$ — $118\cdot2^\circ$ .

CHEMICAL ABSTRACTS.

## Physiological Chemistry.

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**Further Data Concerning the Alleged Relation of Catalase to Animal Oxidations.** RAYMOND L. STEHLE and ARTHUR C. McCARTY (*J. Biol. Chem.*, 1920, **42**, 269—272. Compare A., 1919, i, 561).—Measurements were made of the carbon dioxide production, and hæmoglobin and catalase contents of rabbit and cat blood drawn to correspond as nearly as possible with successive periods of normal and high metabolism. Contrary to Burge's hypothesis (compare A., 1919, i, 233), these experiments demonstrate that there may be great variations in the rate of animal metabolism without any change in the catalase content of the blood. W. G.

**Manganese Content of Human Blood and Tissues.** CLARENCE K. REIMAN and ANNIE S. MINOT (*J. Biol. Chem.*, 1920, **42**, 329—345).—See this vol., ii, 558.

**Exchange of Chloride Ions and of Carbon Dioxide between Blood Corpuscles and Blood Plasma.** L. S. FRIDERICIA (*J. Biol. Chem.*, 1920, **42**, 245—257).—The author confirms the results of Van Slyke and Cullen (*A.*, 1917, i, 521) as to the influence of the carbon-dioxide tension on the partition of the chlorides between plasma and red corpuscles, and shows that the cause of the exchange of chloride ions between plasma and corpuscles is in the red corpuscles and not in the plasma. The amount of chloride ions passing from the plasma into the corpuscles by increasing the carbon-dioxide tension from 0.08 to 162 mm. almost completely accounts for the increased carbon-dioxide combining power gained by the plasma. Increasing carbon-dioxide tension increases the carbon-dioxide combining power of both plasma and corpuscles, but the hydrogen-ion concentration remains almost the same in plasma and corpuscles at different carbon-dioxide tensions. Hasselbach's explanation of the properties of hæmoglobin (*A.*, 1917, i, 490) offers an interpretation of both of these phenomena.  
W. G.

**Metabolism of Carbohydrates. I. Stereochemical Changes undergone by Equilibrated Solutions of Reducing Sugars in the Alimentary Canal and in the Peritoneal Cavity.** JAMES ARTHUR HEWITT and JOHN PRYDE (*Biochem. J.*, 1920, **14**, 395—405).—See this vol., i, 508.

**The Metabolism of Sulphur. III. The Relation between the Cystine Content of Proteins and their Efficiency in the Maintenance of Nitrogenous Equilibrium in Dogs.** HOWARD B. LEWIS (*J. Biol. Chem.*, 1920, **42**, 289—296).—A study of the relative efficiencies in nutrition of casein, a protein low in cystine content, and of serum albumin, high in cystine content, for dogs. Under conditions of low protein intake, serum albumin is more effective in maintaining nitrogenous equilibrium than is casein. When casein is supplemented by cystine, however, it is as efficient as serum albumin for the maintenance of nitrogenous equilibrium.  
W. G.

**The Fat-soluble Growth-promoting Substance in Lard and Cotton-seed Oil.** AMY L. DANIELS and ROSEMARY LOUGHLIN (*J. Biol. Chem.*, 1920, **42**, 359—362).—Both lard and cotton-seed oil apparently contain appreciable amounts of the fat-soluble growth-promoting substance, as is shown by the growth of rats on a diet containing either of these fats and otherwise devoid of the fat-soluble vitamine.  
W. G.

**Vitamine Studies. V. The Antiscorbutic Properties of Raw Beef.** R. ADAMS DUTCHER, EDITH M. PIERSON, and ALICE BIESTER (*J. Biol. Chem.*, 1920, **42**, 301—310).—Guinea-pigs were fed on a diet of oats, water, and an amount of autoclaved milk sufficient to improve the diet, but insufficient to prevent scurvy. The animals developed scurvy and died. The addition of water extracts of raw, lean beef equivalent to 5, 10, 15, or 20 grams of

beef had no effect on the time of onset of scurvy or on the length of life of the animals. That the beef extract contained no deleterious ingredient was shown by the fact that when orange juice was added to the diet in addition to the beef juice, there was no scurvy and the animals were in excellent condition.

W. G.

**Lipase of Pulmonary Tissue.** ANDRÉ MAYER and PIERRE MOREL (*Bull. Soc. chim. Biol.*, 1919, 1, 189—207).—Pulmonary tissue contains an enzyme which hydrolyses esters and glycerides, and has properties different from those of pancreatic lipase.

J. C. D.

**Action of Extracts of the Spleen on the Smooth Muscle Tissues. Preparation and Nature of the Active Principle.**

L. STERN and E. ROTHLIN (*J. Physiol. Path. gen.*, 1920, 18, 753—780).—The authors attempt to isolate the active principle of extracts of the spleen, which produces hypertonic conditions in organs containing smooth muscle tissue. Fresh spleens were cleaned from fat and connective tissue and ground to a pulp. The macerated tissue was boiled for half an hour in 2 to 3 vols. of water made slightly acid with acetic acid, and filtered. The filtrate was then heated just to the b. p., and sodium chloride and acetic acid were added until no more precipitation occurred. After filtering, the filtrate (usually clear) was evaporated on a water-bath to one-tenth the original volume. The material separating out on cooling was removed by filtration or centrifuging, and the liquid evaporated to dryness, powdered, and kept in a desiccator over sulphuric acid or calcium chloride. The product is soluble in water and very active in producing hypertonicity, 25 to 30 grams of substance result from 1 kilo. of spleen. The ethereal extract of the powder when dried and dissolved in salt solution is ineffective in producing contraction of smooth muscle. An extract of the powder made with slightly acidified ethyl alcohol is, however, quite as active as an equivalent amount of the original preparation. During the evaporation of the ethyl-alcoholic extract, insoluble material settles out, which is removed by filtration or centrifugation, and the residual liquor evaporated to dryness. A dark brown, hygroscopic powder results. The further purification of the compound is best effected by precipitation with phosphotungstic acid, and gives a product some sixty times as effective. The preparation is named "liénine" by the authors, who consider from physiological experiments that its action is through a direct effect on the smooth muscle fibres, thus differentiating it from adrenaline, which acts by intermediation of the nerve elements. Liénine is thus similar in action to  $\beta$ -amino-4-ethylglyoxaline. In view of these results, particular interest is attached to the spleen. It appears as if this organ can be considered as exercising an action on the general economy in retarding the exchanges and counterbalancing the action of other organs,

for example, the thyroid, such splenic function being due, in part at least, to liénine, representing as it does a product of internal secretion or functional activity.

CHEMICAL ABSTRACTS.

### **Evidence Indicating a Synthesis of Cholesterol by Infants.**

JAMES L. GAMBLE and KENNETH D. BLACKFAN (*J. Biol. Chem.*, 1920, **42**, 401—409).—For the estimation of cholesterol in milk and stools, the authors recommend a modification of the method of Autenreith and Funk (*Münch. med. Woch.*, 1913, **60**, 1243), the non-saponifiable material being separated from the soaps by using diluted alcohol and light petroleum (compare Kumagawa and Suto, A., 1908, ii, 331).

Analyses of the non-saponifiable fraction of infants' stools confirm the observation of Müller (compare A., 1900, ii, 289) that in the case of infants on a continued milk diet, cholesterol is excreted in the stools without undergoing change to any appreciable extent into coprosterol. From determinations of the cholesterol intake and excretion of four infants over a period of three days, during which the subjects were gaining in weight and receiving a usual amount of cholesterol, it is shown that the cholesterol excreted was 1.7 to 3.4 times that which was present in the food.

W. G.

### **Decomposition of Propionic Acid in the Animal Body.**

LÉON BLUM and PIERRE WORINGER (*Bull. Soc. chim. Biol.*, 1920, **2**, 88—95).—Lactic and pyruvic acids were found in the urine following the administration of propionic acid to dogs and rabbits. These products probably arise in the body by oxidation of the  $\alpha$ -carbon atom of the injected acid. The authors compare this with the oxidation of the  $\alpha$ -carbon atom in the degradation of the  $\alpha$ -amino-acid molecule in the animal organism. The question whether lactic acid or pyruvic acid is the first to be formed is fully discussed, but an opinion is postponed until further researches have been completed.

J. C. D.

### **The Influence of Chemical Constitution on the Toxicity of Organic Compounds to Wireworms.**

F. TATTERSFIELD and A. W. R. ROBERTS (*J. Agric. Sci.*, 1920, **10**, 199—232).—The authors have examined a very large number of organic compounds with respect to their toxic action on wireworms, and from their results certain general conclusions may be drawn as to the relationship between chemical constitution and toxicity.

The general effect of a class of compounds of the same type is directly determined by the chemical constitution of the type, but the particular effects of individual members of a class are limited by their physical properties, such as volatility. On the whole, aromatic hydrocarbons and their halogen derivatives are more toxic than the aliphatic hydrocarbons and their halogen derivatives. The substituents which influence toxicity most when introduced singly into the benzene ring are, in decreasing order of effective-



ness: methylamino-, dimethylamino-, hydroxy-, nitro-, amino-, iodine, bromine, chlorine, methyl groups. This order is, however, modified in the presence of a second substituent; thus, for example, when there is a methyl group already present in the ring, the order becomes: chlorine (in the side-chain), amino-, hydroxy-, chlorine (in the ring), methyl. When chlorine and hydroxy-groups are present together, they give rise to highly toxic substances, and the association of chlorine and nitro-groups in chloropicrin gives rise to one of the most toxic substances tested. Methyl groups introduced into the amino-group of aniline increase toxicity more than if substituted in the ring.

Compounds with irritating vapours, such as allylthiocarbimide, chloropicrin, benzyl chloride, usually have high toxic values, these values not being closely correlated with the vapour pressures or rates of evaporation of these substances.

There is a fairly close relationship between toxicity and vapour pressure, rate of evaporation, and volatility in the case of compounds of the same chemical type. Thus, in a series of similar compounds, decrease in vapour pressure and volatility is usually associated with an increase in toxicity. A limit is put on toxicity by the decrease in vapour pressure, which may sink too low to permit of a toxic concentration in the vapour phase. Chemically inert compounds boiling above  $170^{\circ}$  are usually uncertain in their toxic effect on wireworms, even after an exposure for 1000 minutes at  $15^{\circ}$ . Nearly all organic compounds boiling above  $215^{\circ}$  are uncertain in their action, whilst those boiling above  $245^{\circ}$  are non-toxic, although these limits depend to some extent on the resistance of the insect, the length of exposure, and the temperature at which the experiment is carried out.

W. G.

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## Chemistry of Vegetable Physiology and Agriculture.

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### Action of a Bulgarian Ferment on Maltose and Sucrose.

GEN ITSU KITA (*Bull. Soc. chim. Biol.*, 1920, **2**, 140—142).—This enzyme has no action on maltose or sucrose, as has previously been stated by Bertrand and Ducháček (*A.*, 1909, i, 623).

J. C. D.

**The Fermentation of Dextrose, Galactose, and Mannose by *Lactobacillus pentoaceticus*, n.sp.** W. H. PETERSON and E. B. FRED (*J. Biol. Chem.*, 1920, **42**, 273—287).—[With J. A. ANDERSON.]—The aldoses, dextrose, galactose, and mannose are fermented by *Lactobacillus pentoaceticus*, n.sp., with the production of lactic acid, ethyl alcohol, carbon dioxide, and small amounts of acetic acid. Dextrose and galactose are fermented at approxim-

ately the same rate and to the same extent, but mannose is more slowly attacked and less sugar is consumed. The difference is probably explicable by the configuration of the sugars.

The acetic acid obtained during the fermentation is probably produced by secondary fermentation of the lactic acid formed.

W. G.

**The Nature of Yeast Fat.** IDA SMEDLEY MACLEAN and ETHEL MARY THOMAS (*Biochem. J.*, 1920, **14**, 483—493).—Palmitic, oleic, and linoleic acids have now been identified with certainty in yeast fat, but the pentadecic acid previously described (Hinsberg and Roos, A., 1903, ii, 565; 1904, ii, 760) is a mixture of palmitic and lauric acids. An acid, m. p.  $77^{\circ}$ , was isolated (compare Neville, A., 1913, i, 1026), and is possibly arachidic acid. The authors were unable to confirm the presence of the dodecenoic acid described by Hinsberg and Roos (*loc. cit.*).

The sterol, present to the extent of about 20% of the total yeast, being partly in the free state and partly as fatty acid esters, is apparently identical with Tanret's ergosterol (A., 1889, 407). It is probable that the mycosterol isolated from certain fungi by Ikeguchi (this vol., i, 160) is also identical with ergosterol, and that this sterol is characteristic of the whole group of cryptogams. Yeast sterol is differentiated from the sterols of the higher plants and animals by the presence of three double bonds in its molecule.

W. G.

**Water Culture Experiments with Different Nutrient Solutions; Influence of Manganese and Hydrogen-ion Concentration.** FR. WEIS (*K. Vet.-Landbohøjskole Aarsskrift.*, 1919, 239—280; from *Chem. Zentr.*, 1920, iii, 99).—Manganese sulphate added to culture solutions in an amount equivalent to their normal iron content does not exert a beneficial influence on the growth of plants. The most favourable hydrogen-ion concentration for the classes of plants investigated was  $p_H = 4.5-6.0$ .

H. W.

**Action of Chromium and Manganese on Plant Growth.** TH. PFEIFFER, W. SIMMERMACHER, and A. RIPPEL (*Fühlings Landw. Zeit.*, 1918, **17/18**, 313; from *Bied. Zentr.*, 1920, **49**, 259—263).—Experiments on oats and barley treated with an ordinary fertiliser and with small proportions of chrome iron ore or potassium dichromate fail to reveal any beneficial effect of the chromium (compare König, A., 1911, ii, 524). Similar experiments on oats treated with manganous sulphate indicate that the effect of the manganese is at most very minute.

T. H. P.

**Are Vitamines Necessary for the Development of Plants?** AUGUSTE LUMIERE (*Compt. rend.*, 1920, **171**, 271—273).—The author finds that fresh brewer's yeast heated to  $135^{\circ}$ , and no longer capable of curing polyneuritis in pigeons, gives a bouillon which considerably improves the development of fungi grown on poor culture solutions. As a result of these and further experiments, the

author concludes that vitamins, as ordinarily characterised, are not essential for the development of plants. W. G.

**Chemical Components of Green Plants. II. Presence of a Mixture of Unsaturated Alcohols in many Green Plants.**

HARTWIG FRANZEN and ADOLF WAGNER (*Sitzungsber. Heidelberg Akad. Wiss. Math. nat. Klasse*, Abt. A, 1920, 2 reprints, pp. 4; from *Chem. Zentr.*, 1920, iii, 95).—The mixture of unsaturated alcohols found previously in the leaves of beech and chestnut is shown by its characteristic odour to be present also in the leaves of all classes of plants investigated (forty have been examined). The distillate from the mountain ash also contained hydrocyanic acid, whilst a component with an intense odour of lemons (citral) was present in that from strawberry leaves. The first distillate from certain plants (wormwood, dahlia, peppermint, ivy) contained notable amounts of essential oils. H. W.

**The Presence of Copper in Plants and Particularly in Foodstuffs of Vegetable Origin.** B. GUÉRITHAULT (*Compt. rend.*, 1920, 171, 196—198).—The author has determined the percentage of copper present in a large number of fruits, vegetables, and seeds, and finds that the amount varies from 0.0087 to 0.0636% of the ash, and from 1.1 to 17.1 mg. per kilo. of fresh material. W. G.

**The Odorous Constituents of Apples. Emanation of Acetaldehyde from the Ripe Fruit.** FREDERICK B. POWER and VICTOR K. CHESNUT (*J. Amer. Chem. Soc.*, 1920, 42, 1509—1526).—The odorous constituents of apples were found to consist essentially of the amyl esters of formic, acetic, and hexoic acids, with a very small amount of the octoic ester. In addition, there was a considerable proportion of acetaldehyde and probably some free acid. The aqueous distillate from fresh apple parings also contained exceedingly small amounts of methyl and ethyl alcohols and furfuraldehyde, the latter probably arising from some chemical change during the distillation. The essential oil obtained from apple parings amounted to 0.0035% in the case of Ben Davis apples and 0.0043% in the case of crab apples.

Acetaldehyde is a product of the vital activities of the fruit, and occurs in the exhalations from ripe apples. W. G.

**The Extraction of the Fat-soluble Factor of Cabbage and Carrot by Solvents.** SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1920, 14, 494—501).—Alcohol extracts the fat-soluble factor from cabbage and carrots. An amount of such extract equivalent to 10—12 grams of fresh carrots given daily is sufficient to promote normal growth in rats subsisting on a diet lacking the fat-soluble factor. In addition, the alcoholic extract from carrots contains the antineuritic and, to a smaller extent, the antiscorbutic factors. An ethereal extract from the alcoholic fraction equivalent to 25 grams of fresh carrots promoted recovery and renewed growth in rats

which were declining in weight on account of a fat-soluble factor deficiency. W. G.

**The Occurrence of Water-soluble Vitamine in some Common Fruits.** THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*J. Biol. Chem.*, 1920, **42**, 465—489).—[With ALFRED J. WAKEMAN.]—The fresh juices of the edible parts of the orange, lemon, and grapefruit contain water-soluble *B* vitamine, the potency of the juices in this respect being similar, for equal volumes, to that of cow's milk. These juices may be suitably desiccated on starch without losing their efficiency. Grape juice was less potent than the fruit juices mentioned above. The edible portions of apples and pears furnish some water-soluble *B*, but from a comparative standpoint they cannot be regarded as rich in this factor; prunes are apparently somewhat richer.

From preliminary experiments it is doubtful whether the juices of lemon or grapefruit contain more than traces, if any, of the fat-soluble vitamine, though orange-juice would appear to contain some of this vitamine. W. G.

**Spilanthol, the Pungent Principle of Para Cress (*Spilanthes oleracea*).** I. YASUHIKO ASAHINA and MICHIZÔ ASANO (*J. Pharm. Soc. Japan*, 1920, No. 460, 503—515).—Gerber (A., 1903, ii, 609) isolated the pungent principle of Para cress, spilanthol,  $C_{37}H_{64}O_3N_2$ , as a syrup, which, when heated with alcoholic hydrochloric acid in a sealed tube, gave a base,  $C_4H_{11}N$ , and an acid,  $C_{14}H_{28}O_2$ . The authors prepared crude spilanthol (about 1%) from the air-dried flower-heads of the plant by Gerber's method. When kept it is changed into a resinous substance, and it becomes less soluble in ether. The base,  $C_4H_{11}N$ , formed by heating it with alcoholic hydrochloric acid, proved to be *isobutylamine*. Another decomposition product polymerised to a resinous substance. By shaking crude spilanthol in acetic acid solution in presence of platinum-black, it absorbs hydrogen gradually, with formation of *hydrospilanthol*; this is a colourless, viscous liquid with hay-like odour and bitter taste, which solidifies to crystals, m. p.  $28^\circ$ , is stable towards permanganate, and does not polymerise. It is probably a mixture of two substances,  $C_{13}H_{27}ON$  and  $C_{14}H_{29}ON$ . By heating with alcoholic hydrogen chloride in a sealed tube, hydrospilanthol yields *isobutylamine* and a saturated fatty acid, m. p.  $28^\circ$  and b. p.  $136\text{--}140^\circ/4\text{ mm.}$ ; probably a mixture of decoic acid, m. p.  $31\cdot5^\circ$ , and nonoic acid, m. p.  $12\cdot5^\circ$ . K. K.

**The Toxicity of Iron and the Antitoxic Properties of Copper with Respect to Ferrous Salts.** L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1920, **171**, 218—222).—Ferrous salts are much more injurious to young plants than ferric salts. Any condition which tends to facilitate the oxidation of the ferrous to ferric salt consequently diminishes the toxicity of ferrous salts. This is the case with an addition of monopotassium phosphate, and particularly with an addition of copper sulphate, which has been

shown to exert a catalytic action on the oxidation of ferrous salts (compare this vol., ii, 547). W. G.

**Comparative Study of the Microflora and Nitrogen Content of Soils Partly Sterilised by Calcium Sulphide.**

G. TRUFFAUT and N. BEZSSONOFF (*Compt. rend.*, 1920, 171, 268—271).—With a strong application of calcium sulphide and naphthalene or cymene to soil in porous pots, without a crop, this aerobic medium favours losses of ammoniacal nitrogen and is unfavourable to the development of anaerobic bacteria, such as *Bacillus butyricus*. If the experiment is repeated with a crop present, there is much less loss of nitrogen, whilst if the application is applied to soil in the field, crops being grown, it is found that there is a large increase in growth on the treated plot, no loss of nitrogen from the soil, and a considerable increase in the numbers of *B. butyricus* present. W. G.

**Measure of the Ammonising Power of Arable Soil.**

R. PEROTTI (*Atti R. Accad. Lincei*, 1920, [v], 29, i, 251—256. Compare A., 1908, ii, 124).—The best conditions for carrying out the solution method of determining the ammonising power of arable soil are as follows: 10 c.c. of 1.5% peptone solution are treated in a test-tube with 5 c.c. of the solution, obtained by steeping 50 grams of the soil in 500 c.c. of well-water. The tube is kept in a thermostat at 20—25° for four days, after which the ammonia produced is estimated by distilling the contents of the tube in presence of magnesium oxide. The mean of four separate determinations is taken. T. H. P.

**The Mechanism of the Decomposition of Cyanamide in the Soil.**

G. A. COWIE (*J. Agric. Sci.*, 1920, 10, 163—176. Compare A., 1919, i, 376).—Cyanamide decomposes, in untreated soil or in soils previously heated to 120° or 135°, by a purely chemical change to carbamide. The subsequent conversion of the carbamide to ammonia is brought about by soil organisms. In sterile soils there is an accumulation of the carbamide, and this may also occur to a certain extent in soils under normal conditions. This decomposition of cyanamide appears to be more rapid in clay soils than in sandy soils. In the case of an inert sand, in which the cyanamide did not undergo decomposition, it was found that the addition of a zeolite, prehnite, resulted in the conversion of the cyanamide into carbamide.

Cyanamide does not appear to decompose in the manner indicated above in peat and fen soils; in these it gives rise to a relatively small production of carbamide under normal conditions. W. G.

**Solid Phases obtained by the Evaporation of certain Soil Extracts.**

M. S. ANDERSON and WILLIAM H. FRY (*J. Ind. Eng. Chem.*, 1920, 12, 663—668).—The salts deposited on the evaporation of the water extract of soils are of a much more complicated character than is indicated by a simple statement of the ions

existing in solution. The deposited salts are similar to those obtained by natural or artificial evaporation of sea-water, but no soil can be expected to furnish all the salts occurring in natural deposits of saline substances, since these represent crystallisation from a composite soil extract. As the salts begin to separate from the water extract at a point not far from the concentration corresponding with the moisture in an air-dry soil, it follows that the roots of growing plants may be in contact with solutions of these salts. Obversely, it is probable that the complex salts may be present in the soils only in solution in soil moisture, and never in the solid phase.

W. P. S.

**Substances Dissolved in Rain and Snow.** ANON (*Chem. News*, 1920, **121**, 13—14. Compare Schutt and Dorrance, A., 1919, i, 116).—An account of analyses of rain and snow which fell in Mt. Vernon, Iowa, over the period October 9th, 1919, to May 22nd, 1920. During this period, 11·37 inches of rain fell and snow equivalent to 2·07 inches of rain, this in twenty-one precipitations of rain and eight of snow. Mt. Vernon is a town of 2,500 inhabitants, and is situated seventeen miles from the nearest industrial centre; it has no manufacturing industries. The analyses show that, during the period mentioned, 51·0306 lb. of sulphate as  $\text{SO}_3$  fell per acre, the largest amount being 34 parts per million of water on March 4th, or 7·7137 lb. per acre. The total amount of chlorine was 48·1644 lb. per acre, equal to 79·36 lb. of sodium chloride. The largest concentration was in a slight snow storm, equivalent to 0·02 inch of rain, on December 2nd, when 17·7 parts per million were obtained, which is equivalent to 4·0157 lb. per acre. Nitrogen was determined in four forms: as nitrates ( $\text{NO}_3$ ), nitrites ( $\text{NO}_2$ ), free ammonia, and albuminoid ammonia. A total of 0·62841 lb. of nitrogen as nitrate fell, the greatest amount being 0·3 part per million, or 0·06806 lb. per acre, on December 2nd and January 23rd, at which times snow equivalent to 0·08 inch and 0·50 inch of rain fell, respectively. As nitrite, there was a total of 0·03725 lb. per acre, of nitrogen, the greatest amount being on March 19th, equal to 0·02 part per million of water, or 0·00453 lb. per acre; at this time 0·4 inch of rain fell. Free ammonia, equivalent to 2·8642 lb. of nitrogen, fell during the period; on March 4th, nitrogen as ammonia, equal to 2·30 parts per million, or 0·52181 lb. per acre, fell, with 0·4 inch of rain. Albuminoid ammonia was less frequent in its occurrence, for 32% of the rainfalls gave no reactions for this form. A total of 0·4974 lb. of nitrogen as ammonia in the albuminoid form fell, the greatest single amount coming on February 12th, when 1·12 parts of nitrogen per million, or 0·2541 lb. per acre, fell, with snow equal to 0·25 inch of rain. The total amount of nitrogen as free and albuminoid ammonia was 3·3616 lb. per acre. The total amount of nitrogen in all forms was 4·02726 lb. per acre, and of this, 82·5% was in the form of the two ammonias. J. F. S.

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## Organic Chemistry.

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**Weight of a Normal Litre of Propane.** JEAN TIMMERMANS (*J. Chim. physique*, 1920, **18**, 133—141).—Propane was prepared by the action of sodamide on propyl iodide (Lebeau, A., 1905, i, 401, 501) or by the action of sodium on butyronitrile (Stahrfoss, *J. Chim. physique*, 1912, **10**, 497). The weight of a normal litre of the gas, prepared by either method, was found to be 2.0200 grams. W. G.

**Preparation of Propylene and its Homologues.** CHEMISCHE FABRIK BUCKAU (D.R.-P. 294794; from *Chem. Zentr.*, 1920, iv, 222).—A mixture of acetylene and its homologues with methane and its homologues is passed over a suitable non-metallic catalyst at 200—350°. The process may be carried out under increased pressure, or the mixture may be led through a contact apparatus completely filled with a porous catalyst. Titanic and silicic acids and their salts, as well as molybdic and tungstic acids, alumina, thoria, and zirconia, are recommended as catalysts. Examples are cited of the preparation of propylene from acetylene and methane, of butylene from acetylene and ethane, and of  $\Delta\beta$ -butylene from allylene and methane. H. W.

**Conversion of Acetylene into Acetaldehyde and Acetic Acid.** B. NEUMANN and H. SCHNEIDER (*Zeitsch. angew. Chem.*, 1920, **33**, 189—192).—For the conversion of acetylene into acetaldehyde on the laboratory scale, the best results were obtained by leading the gas, with vigorous mechanical stirring, into a catalyst composed of 96% acetic acid containing 3% of mercuric sulphate in solution, the temperature being maintained at about 30°. Under these conditions, nearly 90% of the theoretical yield was obtained. At 40—50°, the rate of absorption was actually greater, but the percentage yield of acetaldehyde was reduced to 70—80. Using a dilute sulphuric acid medium instead of acetic acid, the reaction was more erratic, and, in favourable circumstances, only 70—75% yields were obtained. The optimum temperature in this case was 25—30°, and a very great decrease in the rate of absorption and increase in the formation of polymerised and resinous by-products was observed when the temperature was raised at all above this point. The best results in the direct conversion of acetylene into acetic acid were obtained by using the above mercuric sulphate-acetic acid catalyst with the addition of vanadium pentoxide, acetylene and oxygen being led in alternately. Yields of acetic acid up to 83% were obtained. G. F. M.

**Action of  $\alpha\beta$ -Chloriodo-, Bromiodo-, and Di-iodo-ethanes on the Sodium Sulphides.** MARCEL DELÉPINE and LUCIEN VILLE (*Bull. Soc. chim.*, 1920, [iv], **27**, 678—679).—When sodium sulphide acts on  $\alpha\beta$ -chloriodo-, bromiodo-, or di-iodo-ethane in



aqueous or aqueous-alcoholic solution, ethylene, sulphur, and the sodium haloids are produced:  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\text{I} + \text{Na}_2\text{S} = \text{NaCl} + \text{NaI} + \text{S} + \text{C}_2\text{H}_4$ . A similar reaction occurs if sodium hydrogen sulphide is used in place of the neutral sulphide. W. G.

**Formation of Chlorohydrins. III.** L. SMITH and E. SAMUELSSON (*Zeitsch. physikal. Chem.*, 1920, **94**, 691—722. Compare A., 1918, i, 370).—The present paper deals with the formation of monochlorohydrin, and is divided into two portions; the first deals with the formation from glycerol and hydrogen chloride, whilst the second treats of the action of hydrogen chloride on glycide. In the first case, twenty-three syntheses have been effected, with yields varying from 10—70% of the monochlorohydrin. It is shown that the lower the temperature the greater the yield of the  $\alpha$ -chlorohydrin, and this is more noticeable if water is present from the beginning of the operation. Higher temperatures operate in the reverse way up to a certain point, which is probably to be explained by side reactions. In other words, the velocity with which hydrogen chloride attacks the secondary hydroxyl group has a greater temperature-coefficient than the velocity of the isomeric reaction. In the presence of succinic acid, and probably other catalysts, the  $\alpha$ -isomeride is the chief product, whilst water, which retards the reaction, increases the yield of the  $\beta$ -isomeride. The catalyses by raising the temperature and by succinic acid are therefore opposed to one another. At those temperatures where the  $\beta$ -isomeride is formed in appreciable quantity, it is also decomposed rapidly, and much more so than its isomeride. It is possible by the following method to obtain a 40% yield of the pure  $\alpha$ -isomeride: 0.5 gram-mol. of anhydrous glycerol containing 2 grams of succinic acid is treated with hydrogen chloride at  $18^\circ$  until there is an increase in weight of 18 grams. The addition of the hydrogen chloride takes place in two stages, with a pause of a day between the two additions. It is probable that a larger yield would be obtained if the mixture was kept longer. The unattacked glycerol may be regained in probably quantitative yield by distillation. The highest yield of the  $\beta$ -isomeride obtained was 15%. The best laboratory method for the preparation of glyceryl  $\alpha$ -monochlorohydrin of approximate purity (1%  $\beta$ -isomeride) appears to be the following. Hydrogen chloride is passed into 1 gram-mol. of glycerol containing 4 grams of succinic acid until the weight has increased by 47 grams. The addition requires about eight hours, and the heat of the reaction keeps the temperature at  $60$ — $70^\circ$ . The mixture should then be kept overnight. The yield in this case is 70%. If no special demands on the uniformity of the product are made, the reaction may be carried out at  $120^\circ$  until 39 grams of hydrogen chloride have been added. This gives a yield of 65%, and is much more conveniently carried out than the other methods.

The action of hydrogen chloride on glycide has been carried out in the following way: (i) leading hydrogen chloride into the pure glycide at  $-15^\circ$ ,  $100^\circ$ , and  $140$ — $145^\circ$ ; (ii) leading hydrogen

chloride in ethereal solutions of the glycide at  $-76^{\circ}$ ,  $-15^{\circ}$ , and  $25-27^{\circ}$ ; (iii) dropping the glycide into (a) ethereal solutions of hydrogen chloride, (b) acetone solutions of hydrogen chloride, and (c) concentrated hydrochloric acid, at  $-76^{\circ}$ ,  $-14^{\circ}$ ,  $25-30^{\circ}$ ,  $50-55^{\circ}$ . The reaction velocity has been ascertained in each case. It is shown that at very low temperatures the chlorine enters the  $\alpha$ -position by preference, but the reaction is never simply this, some of the  $\beta$ -isomeride always being produced. J. F. S.

**Glyceryl  $\beta$ -Monochlorohydrin.** L. SMITH (*Zeitsch. physikal. Chem.*, 1920, **94**, 723-738. Compare preceding abstract).—After discussion of a number of methods for the preparation of glyceryl  $\beta$ -chlorohydrin, the author recommends the following method of procedure. A mixture of 97 grams of 95% glycerol and 150 grams of concentrated hydrochloric acid is heated for five hours at  $120^{\circ}$ . This is then distilled at a pressure of 15 mm., and the fraction distilling at  $110-150^{\circ}$  collected. This fraction is pure chlorohydrin, and contains 14-15% of the  $\beta$ -isomeride. The product is purified by a long-continued fractional distillation under reduced pressure. The following physical properties are recorded: boiling point,  $\alpha$ -isomeride,  $119-119.5^{\circ}/14.5$  mm.,  $\beta$ -isomeride,  $124.5-125^{\circ}/14.5$  mm.;  $\beta$ -isomeride,  $D_0^{20}$  1.3375,  $D^{20}_{20}$  1.3207;  $\alpha$ -isomeride,  $D^{20}_{20}$  1.3213. The molecular weight by the cryoscopic method in water solution is 113 (theory, 110.5). J. F. S.

**The History of Alcohol.** EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1920, **44**, 625. Compare A., 1913, i, 155, 244, 1298; 1918, i, 210).—The recent publication of Sudhoff confirms the author's previous conclusion that the distillation of alcohol was first effected in connexion with that of rose-water and not, apparently, by the followers of any official medical school. Distilled alcohol does not appear to have been made before the middle of the twelfth century. H. W.

**Refractive Indices of Mixtures of isoPropyl Alcohol and Acetone.** DOROTHY MURIEL PALMER (*Analyst*, 1920, **45**, 302).—Tables are given showing the refractive indices of mixtures of acetone and isopropyl alcohol containing from 0 to 100% of the latter. W. P. S.

**Chloroformic Esters.** G. CAPELLI (*Gazzetta*, 1920, **50**, ii, 8-12).—In order to obtain chloroformic esters in good yield by the action of carbonyl chloride on an alcohol, the former reagent must always be present in considerable excess. Good results may be obtained by using furnace coke, which is carefully dried, broken into pieces the size of peas, cooled by means of pounded ice, and saturated with carbonyl chloride. The flow of the gas is subsequently increased and the alcohol added in rapid drops. In order that the whole of the alcohol may be converted into ester and that the excess of carbonyl chloride may escape, the crude ester is left in a strong draught for about twenty hours, and is then

washed with ice-water, dried by means of calcium chloride, and fractionally distilled. The use of basic substances is unnecessary and the alcohol need not be anhydrous, 90% yields being obtained from alcohol of 76% concentration.

T. H. P.

**Improvements in Methods of Forming Esters.** U.S. INDUSTRIAL ALCOHOL Co. (Brit. Pat. 147337).—Esters of the higher alcohols are produced by partial esterification in presence of a dehydrating agent, separating the latter, and continuing the esterification at a higher temperature. For instance, a mixture of 3205 grams of fusel oil (D 0.8268), 256 grams of concentrated sulphuric acid, and 2564 grams of glacial acetic acid is kept for twenty-four hours at the ordinary temperature with occasional agitation. The aqueous layer containing all the sulphuric acid is separated, and the oily layer distilled at 100° until no further separation of water occurs, indicating that esterification has ceased. The oily layer in the distillate is from time to time separated from the water and returned to the still, the contents of which are finally neutralised with 30% sodium hydroxide solution. The sodium acetate layer which separates is drawn off and distilled at 100° to recover any amyl acetate it may contain.

G. F. M.

**Anomalies in the Solidification Point of Tristearin.** BEN H. NICOLET (*J. Ind. Eng. Chem.*, 1920, **12**, 741—743).—The double melting point of tristearin is attributed to the existence of two modifications, the more stable of which has m. p. 71.6—72.2°, and the unstable form about 55°, the latter being reconverted into the stable form on heating it at a higher temperature or allowing it to remain. In spite of the speed of solidification, the solidification point of tristearin is usually given as that of the unstable form (about 55°). The solidification point of pure tristearin was determined by the rise of temperature in Dalican's method. It first showed signs of solidification at 53.8°; the temperature then rose normally to about 63.5°, remained almost constant for some time, and then rose rapidly to the maximum at about 69°. On "seeding" liquid tristearin with the stable modification above 60°, solidification takes place without the formation of the unstable form, but the latter is apparently always produced after seeding, even with the stable form, at temperatures below 56°. Double solidification points are not necessarily shown by all the triglycerides which show a double melting point. It appears to be an essential condition that the solidification of the unstable form shall produce sufficient heat to reach the temperature of transition into the stable form. The phenomenon was shown by hydrogenated soya bean oil, but not by hydrogenated linseed or cotton-seed oil. The solidification point of hydrogenated linseed oil (65.9°) was not raised by "seeding."

C. A. M.

**Fat Associated with Starch.** T. C. TAYLOR and J. M. NELSON (*J. Amer. Chem. Soc.*, 1920, **42**, 1726—1738).—Corn starch, carefully freed from adherent or associated fat by repeated extraction

with ether, light petroleum, and carbon tetrachloride, gave on hydrolysis a material from which fat or free fatty acids could be extracted. The principal constituent of this "fat by hydrolysis" was palmitic acid, but there was, in addition, an unsaturated compound of unknown constitution. By controlled acid hydrolysis it was found that this fat was liberated when the hydrolysis had reached the erythrodextrin stage. Fat is also obtained by diastatic hydrolysis or hydrolysis with *Bacillus aceto-ethylicum*. By controlling the hydrolysis of the starch, it is possible to obtain residues containing relatively large amounts of fat combined with carbohydrate. Analytical data indicate that the palmitic acid is probably attached directly to the unsaturated compound mentioned above in the form of an ester. Starches from other vegetable sources also contained varying amounts of "fat by hydrolysis," the amounts obtained varying from 0.04—0.83%.  
W. G.

**Photochemical Chlorination of Methyl Sulphate. Preparation of Chloromethyl Sulphate.** VOLMAR (*Bull. Soc. chim.*, 1920, [iv], 27, 681—684).—Methyl sulphate readily undergoes chlorination at the ordinary temperature under the influence of ultra-violet rays, and more slowly under the influence of the light from an arc lamp or a metal filament lamp. The product is, in all cases, methyl chloromethyl sulphate,  $\text{CH}_3\text{Cl} \cdot \text{MeSO}_4$ . The fixation of a second chlorine atom is not possible, because it requires radiations of such a wave-length that the dichloromethyl sulphate is decomposed as it is formed.  
W. G.

**Catalytic Oxidation by Unsaturated Compounds (Oils, Hydrocarbons, etc.).** J. BOUGAULT and P. ROBIN (*Compt. rend.*, 1920, 171, 353—355).—When a solution of  $\beta\beta'$ -dichlorodiethyl sulphide in turpentine is exposed to air, the sulphide undergoes oxidation, giving  $\beta\beta'$ -dichlorodiethyl sulphoxide,  $\text{SO}(\text{C}_2\text{H}_4\text{Cl})_2$ , m. p.  $112^\circ$ , which, when oxidised with potassium permanganate in acid solution, gives  $\beta\beta'$ -dichlorodiethylsulphone,  $\text{SO}_2(\text{C}_2\text{H}_4\text{Cl})_2$ , m. p.  $55^\circ$ , and when treated with aqueous potassium hydroxide gives  $\beta\beta'$ -dihydroxydiethyl sulphoxide,  $\text{SO}(\text{C}_2\text{H}_4 \cdot \text{OH})_2$ , m. p.  $111^\circ$ . The turpentine may be replaced by various unsaturated oils and hydrocarbons. Similarly, when  $\beta\beta'$ -dihydroxydiethyl sulphide in solution in citraldehyde is exposed to air, it gives the dihydroxydiethyl sulphoxide described above.

That these oxidations are due to the catalytic action of the unsaturated solvents is shown by the fact that  $\beta\beta'$ -dichlorodiethyl sulphide in the pure state or in solution in a saturated oil does not undergo oxidation when exposed to air.  
W. G.

**Triethylene Tri- and Tetra-sulphides.** (SIR) PRAFULLA CHANDRA RÂY (T., 1920, 117, 1090—1092).

**Optical Rotation of Dextrose under the Influence of Hydrochloric or Sulphuric Acid. I.** HANS MURSCHAUSER (*Biochem. Zeitsch.*, 1920, 104, 214—236).—Experiments with

hydrochloric acid at the ordinary temperature indicate that the influence of acid on the mutarotation of dextrose consists in an acceleration of the reaction to an extent increasing with the concentration of the acid; the accelerating effect of sulphuric acid is less than that of hydrochloric acid. The value of the final specific rotation increases with the proportion of acid present in the solution. Especially when the acidity is low, the rotation of dilute dextrose solutions is affected by hydrochloric acid less than that of more concentrated solutions. With the 10% acid, the specific rotation remains constant for a long time independently of the concentration; with the 20% acid, the rotation of dilute dextrose solutions does not change over a long period, but that of the more concentrated solutions gradually rises; 30% of hydrochloric acid produces a permanent increase in the rotation, this being greater for the high than for the low concentrations; 46% of the acid causes an initial increase in the rotation for the higher concentrations of the sugar, but continuous fall in the rotation soon begins, owing to decomposition of the dextrose.

T. H. P.

**Action of the Carbonates of the Alkaline Earths on Dextrose. II. Dextrose and Calcium Carbonate.** HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1919, **99**, 190—204).—The modified dextrose obtained by boiling a solution of dextrose with calcium carbonate for three hours (this vol., i, 13) is fermentable. The presence of lævulose in it was demonstrated by Selivanov's reaction and by the separation of lævulose phenylmethyllosazone by Neuberg's method.

S. S. Z.

**Dry Distillation in a Vacuum and its Application to the Study of Carbohydrates.** AMÉ PICTET (*Bull. Soc. chim.*, 1920, [iv], **27**, 641—656).—A lecture delivered before the French Chemical Society.

**The Ethylene-oxide Structure of Sucrose and some other Carbohydrates.** EDWARD FRANKLAND ARMSTRONG and THOMAS PERCY HILDITCH (*T.*, 1920, **117**, 1086—1090).

**Cellulose Acetate.** H. J. H. FENTON and A. J. BERRY (*Proc. Camb. Phil. Soc.*, 1920, **20**, 16—22).—The work described was mainly on the lines of investigating (a) substitutes for acetone as a solvent; (b) the influence of the mode of preparation on the properties of the product; (c) the characterisation and analysis of cellulose acetate.

No general conclusion can be drawn as regards the chemical nature of a liquid and its solvent action on cellulose acetate, although there appears to be some relation between the dielectric constant and solvent action. The authors consider that in Miles's method for the conversion of the cellulose acetate from an insoluble to an acetone-soluble form, partial hydrolysis, and not hydration, occurs. For the estimation of the acetyl group, the authors prefer Ost's method of cold alkaline hydrolysis (*A.*, 1912, i, 680).

W. G.

**The Supposed Degradation of Starch by means of Formaldehyde.** J. WOHLGEMUTH (*Biochem. Zeitsch.*, 1919, **99**, 316—320).—A final reply to Woker's criticism (this vol., i, 689).  
S. S. Z.

**Iron Salt of Carbohydrate-Phosphoric Acid.** KARL SCHWEIZER (*Bull. Assoc. chim. Sucr.*, 1920, **37**, 464—468).—See this vol., i, 531.

**Synthesis of Phytic Acid.** R. J. ANDERSON (*J. Biol. Chem.*, 1920, **43**, 117—128).—The reaction between inositol, phosphoric acid, and phosphoric oxide has been again studied (compare Posternak, A., 1919, i, 433). The main product of this reaction appears to be an inositol ester of pyrophosphoric acid containing 4 atoms of phosphorus or 2 mols. of pyrophosphoric acid, and corresponding with the formula  $C_6H_{12}O_{16}P_4$ . This does not agree with the conclusion reached by Posternak (*loc. cit.*), who believed the chief product to be identical with the natural phytic acid or inositol-hexaphosphoric acid,  $C_6H_{18}O_{24}P_6$ .  
J. C. D.

**Complex Metallic Ammines. IV. *cis*-Sulphoacetato-, *cis*-Methionato-, and *cis*-Dimethylmalonato-diethylenediaminecobaltic Salts.** THOMAS SLATER PRICE and JAMES COOPER DUFF (T., 1920, **117**, 1071—1077).

**$\psi$ -Muscarine ("Synthetic Muscarine").** ALBERT B. WEINHAGEN (*J. Amer. Chem. Soc.*, 1920, **42**, 1670—1678).—The action of nitric acid on choline platinichloride, according to the original directions of Schmiedeberg and Harnack (*Arch. exp. Path. Pharm.*, 1877, **6**, 101), gives as the principal product the platinichloride of choline nitrite (compare Ewins, A., 1914, i, 665), and in addition a compound, m. p. 204—205°, which is probably dimethylaminoethyl nitrate platinichloride and trimethylamine platinichloride. By deviating from the original directions by evaporating five times with nitric acid instead of only once, choline nitrite was not obtained, the main products being trimethylamine platinichloride and a compound, m. p. 208°, probably having the constitution  $[NMe_2 \cdot CH_2 \cdot CH(OH)_2]_2PtCl_6$ , assigned by Schmiedeberg and Harnack (*loc. cit.*) to "synthetic muscarine." In addition to the platinichloride, the derivatives of choline nitrite obtained were the *hydrochloride*, m. p. 165°, the *aurichloride*, the *sulphate*, the *perchlorate*, and the *free base*.

The pharmacological effects of "synthetic muscarine" reported by different observers must be considered with the above facts in mind.  
W. G.

**Manufacture of Complex Silver Salts of Aliphatic  $\alpha$ -Amino-acids.** HERMANN RICHARD NAPP (Brit. Pat. 148074).—Complex silver salts of aliphatic  $\alpha$ -amino-acids are obtained by dissolving freshly precipitated silver oxide, or organic or inorganic salts of silver, in a solution containing an excess of the amino-acid

and allowing to crystallise, after suitable evaporation, if necessary, except in the case of the glycine compound, where crystallisation must be effected at temperatures below  $0^{\circ}$ , or otherwise the normal silver salt is obtained. These complex salts are more stable and more readily soluble in water than the normal salts, and do not give all the reactions of the silver cation, sodium hydroxide or carbonate, for instance, giving no immediate precipitation. The aqueous solutions are alkaline to litmus and do not precipitate albumin. The compounds have no irritating effect, and this, together with their other properties, renders them suitable for therapeutic purposes.

G. F. M.

### Decomposition of Glutamic Acid and its Salts on Heating.

VLAD ŠKOLA (*Zeitsch. Zuckerind. Cechoslov.*, 1920, **44**, 347—351, 355—360, 363—368, 370—374).—Glutamic acid melts at  $211^{\circ}$  when very rapidly heated; when heated more slowly, or after prolonged drying at  $110^{\circ}$ , it shows a lower m. p., owing to slight decomposition (compare Menozzi and Appiani, *A.*, 1894, i, 498). The conversion of *d*-glutamic acid into its lactam, *l*-glutimic acid (Staněk, *A.*, 1912, i, 952), probably takes place to a slight extent when the former is simply dissolved in water. Equilibrium is attained in 2% solution after boiling for 100 hours, and 90—95% of glutimic acid is formed. The reaction is unimolecular. In presence of sulphuric or hydrochloric acid, the equilibrium is displaced in favour of glutamic acid; the displacement is a function of the concentration of mineral acid, and is much greater with hydrochloric than with sulphuric acid at the same concentration. Glutimic acid found in products of protein hydrolysis may thus be a secondary product only, and its amount may vary according as sulphuric or hydrochloric acid was used as hydrolyst. The pyrrolidone-2-carboxylic acid formula for glutimic acid is confirmed by the author's observation that this acid does not react with formaldehyde by Sørensen's method. The nitrogen of glutamic acid, on the other hand, reacts almost quantitatively provided that successive additions of formaldehyde are made alternating with neutralisation of the acidity developed by each addition. [See also *J. Soc. Chem. Ind.*, 1920, Oct.] J. H. L.

**Synthesis of a Second Diamide, Oxamide, by Oxidation of Sucrose and Ammonia.** R. FOSSE (*Compt. rend.*, 1920, **171**, 398—400).—When a solution of sucrose in strong ammonium hydroxide is oxidised by calcium permanganate, oxamide is obtained, and the course of the reaction is considered to be  $2\text{CH}_2\text{O} \rightarrow 2\text{HCN} \rightarrow (\text{CN})_2 \rightarrow (\text{CO}\cdot\text{NH}_2)_2$ .

W. G.

**The Constitution of Carbamides. XI. The Mechanism of the Synthesis of Urea from Ammonium Carbamate. The Preparation of certain Mixed Tri-substituted Carbamates and Dithiocarbamates.** EMIL ALPHONSE WERNER (*T.*, 1920, **117**, 1046—1053).

**The Constitution of Carbamides. XII. The Decomposition of Urea when Heated in Solution in the Presence of Acids.** EMIL ALPHONSE WERNER (T., 1920, 117, 1078—1081).

**The Nature of the  $\beta$ -Ferricyanides and the  $\beta$ -Ferrocyanides.** SAMUEL HENRY CLIFFORD BRIGGS (T., 1920, 117, 1026—1034).

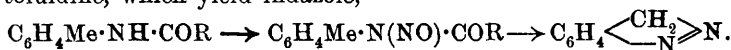
**Estimation of Active Hydrogen in Organic Compounds.** R. CIUSA (*Gazzetta*, 1920, 50, ii, 53—55).—The method suggested by Moureu and Mignonac for diagnosing amines by treating them with magnesium ethyl bromide in ethereal solution and measuring the volume of ethane formed (A., 1914, i, 808) was first suggested by Tschugaev (A., 1903, i, 79) for the determination of the atoms of active hydrogen.

The author applies Moureu and Mignonac's experimental conditions to methyl alcohol, phenol, resorcinol,  $\alpha$ -naphthol, pyrrole, 2-methylindole, phenylbenzylidenehydrazine, ethyl acetoacetate and ethyl ethylacetoacetate, nitromethane and nitroethane, the values obtained for the number of atoms of active hydrogen being either those required or in agreement with the results of previous investigators. 1-Methylpyrrole, 1-methylindole, and trinitrobenzene yielded no gas. T. H. P.

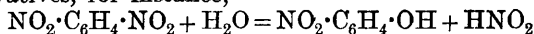
**Reactions of certain Ortho- and Para-substituted Benzene Derivatives.** A. ANGELI (*Gazzetta*, 1920, 50, ii, 1—8; *Atti R. Accad. Lincei*, 1920, [v], 29, i, 375—381).—The author has shown previously (A., 1917, i, 452) that hydrogen peroxide, hydroxylamine, and hydrazine exhibit chemical analogy to quinol, *p*-aminophenol, and *p*-phenylenediamine, and that in some reactions of ortho- and para-substituted aromatic compounds, the two substituent groups behave as though directly joined. Further examples of such analogy are now given.

The reaction between a ketone and ethyl oxalate,  $R \cdot COMe + (CO_2Et)_2 \rightarrow R \cdot CO \cdot CH_2 \cdot CO \cdot CO_2H$ , is quite analogous to that between *o*- or *p*-nitrotoluene and the ester,  $C_6H_4Me \cdot NO_2 + (CO_2Et)_2 \rightarrow NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot CO_2H$ . With the aliphatic compounds, it is the negative group (CO, CN, etc.) which impresses increased mobility on the hydrogen atoms of the methyl group, whereas with the aromatic compounds this purpose is served by the nitro-group, which enhances the negative character of the whole of the aromatic residue.

The hydrolysis of certain methylamine derivatives, with formation of diazomethane,  $NHMe \cdot COR \rightarrow NO \cdot NMe \cdot COR \rightarrow CH_2 \cdot N:N$ , is similar to the behaviour of analogous derivatives of *o*-toluidine, which yield indazole,

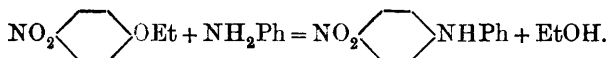


The transformations produced in certain *o*- and *p*-substituted nitro-derivatives, for instance,





and  $\text{NO}_2 \cdot \text{C}_6\text{H}_4\text{Cl} + \text{H}_2\text{O} = \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH} + \text{HCl}$ , correspond with those exhibited by  $\text{N}_2\text{O}_4$  and  $\text{NO}_2\text{Cl}$ . Further, the formation of phenylnitroamine from ethyl nitrate and aniline,  $\text{NO}_2 \cdot \text{OEt} + \text{NH}_2\text{Ph} = \text{NO}_2 \cdot \text{NHPh} + \text{EtOH}$ , is analogous to the reaction



Another group of transformations indicating the connexion between two ortho- or para-substituents is that in which one or both of the oxygen atoms of a nitro-group migrate to a carbon atom. Among these are (1) the formation of *p*-aminobenzaldehyde by the action of alkali sulphide on *p*-nitrotoluene, (2) the conversion of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid under the influence of light, (3) the transformation of *o*-nitrotoluene into *o*-nitrosobenzyl alcohol, and (4) that of *o*-nitrotoluene into anthranilic acid by the action of an alkali. Owing to the marked alterability of the aromatic hydroxylamines and the different behaviour of aliphatic aldehydes and nitro-derivatives, it is not always possible to realise the analogous transformations in the two series, but nitromethane, for instance, readily undergoes the following changes:  $\text{NO}_2\text{Me} \rightarrow \text{OH} \cdot \text{NH} \cdot \text{CHO} \rightarrow \text{NH}_2 \cdot \text{CO}_2\text{H} \rightarrow \text{NH}_3 + \text{CO}_2$ .

A parallel to the oxidation of aliphatic nitro-derivatives,  $2\text{NO}_2 \cdot \text{CH}_2\text{R} \rightarrow \text{NO}_2 \cdot \text{CHR} \cdot \text{CHR} \cdot \text{NO}_2$ , is found with *o*- and *p*-nitrotoluenes, which undergo a similar change without oxidising agents, the oxidation being effected by part of the nitro-compound itself,  $2\text{NO}_2 \cdot \text{C}_6\text{H}_4\text{Me} \rightarrow \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ . In the case of nitromethane, another product, metazonic acid, containing one oxygen atom less, is also obtained.

Analogies also appear between the physiological behaviour of certain corresponding derivatives of the aliphatic and aromatic series. Thus, ethylurethane exerts a hypnotic action, whereas ethyl *p*-aminobenzoate acts as an anæsthetic. Further, hydrazine is poisonous, as also is *p*-phenylenediamine. Aliphatic diamines, such as putrescine and cadaverine, are, however, physiologically inert, and the conclusion is drawn that the same holds for 1:4-diaminocyclohexane.

T. H. P.

**Preparation of Picryl Chloride by Nitration of 4-Chloro-1:3-dinitrobenzene.** PERCY FARADAY FRANKLAND and FREDERIC HORACE GARNER (*J. Soc. Chem. Ind.*, 1920, **39**, 257—260T).—For the preparation of picryl chloride from chlorodinitrobenzene, it is recommended to use 100 grams of chlorodinitrobenzene, 750 grams of 100% sulphuric acid, and 125 grams of 90% nitric acid, the nitration being conducted at 130° for twelve hours. If 96% sulphuric acid is used, the amount must be doubled and the amount of nitric acid increased to 175 grams. A portion of the chlorodinitrobenzene is oxidised, the ratio of the amount of nitric acid used in nitration to the amount used in oxidation being 1:1.8.

W. G.

**Organic Molecular Compounds. IV. Addition of Alkyloxy- to the Nitro-group.** M. GIUA and A. MARCELLINO (*Gazzetta*, 1920, **50**, i, 341—359. Compare A., 1916, i, 205).—In order to ascertain if the property of forming more or less intensely coloured additive compounds with polynitro-derivatives exhibited by aromatic compounds containing a phenolic hydroxyl group persists when the hydroxyl is etherified, the authors have investigated cryoscopically the binary systems formed by *m*-dinitrobenzene, 2:4-dinitrotoluene, 2:4:6-trinitrotoluene, and picric acid with  $\beta$ -naphthol methyl ether and the dimethyl ether of quinol.

The results obtained show that 2:4:6-trinitrotoluene and picric acid, but not *m*-dinitrobenzene or 2:4-dinitrotoluene, form compounds with the ethers mentioned. With the exception of that formed from the dimethyl ether of quinol and picric acid, the nature of the additive compound does not depend on the number of alkyloxy-groups present. Further, the presence of the double ring in  $\beta$ -naphthol is without influence on the formation or non-formation of the additive compound, this observation being in agreement with Sudborough's conclusion that, as regards the property of forming additive compounds, a condensed system of two or more benzene rings may be considered as a single ring (T., 1916, **109**, 1339).

The molecular compounds which 2:4:6-trinitrotoluene and picric acid form with  $\beta$ -naphthol methyl ether and the dimethyl ether of quinol show intense coloration varying from pale yellow to orange-yellow. As in certain similar cases, the colour of the compound is related to the auxochrome group, but for the formation of the compound and of the colour the presence of three nitro-groups in one of the two components is a necessary condition. Which of the three nitro-groups is added to the alkyloxy-group has not yet been established, but from Werner's conception that mutual saturation of the secondary valencies of the chromophore and auxochrome groups must be assumed in the molecular compounds (A., 1910, i, 20), it seems probable that the additive compounds now described are formed by means of the valencies between the characteristic functional groupings; the influence of the aromatic nucleus must not, however, be overlooked. These results are discussed in relation to those obtained by Giua and Cherchi (this vol., i, 303).

The system *m*-dinitrobenzene: $\beta$ -naphthol methyl ether forms a single eutectic, m. p. about 42°, containing 50% by weight of the nitro-compound. 2:4-Dinitrotoluene :  $\beta$ -naphthol methyl ether, one eutectic, m. p. about 34°, 57% of nitro-compound. 2:4:6-Trinitrotoluene :  $\beta$ -naphthol methyl ether forms a compound, m. p. about 73°, containing 1 mol. of each component; the eutectic between the compound and the trinitrotoluene has m. p. about 60°, and that between the compound and the ether m. p. 58°. Picric acid (1 mol.) and  $\beta$ -naphthol methyl ether (1 mol.) form a compound, m. p. about 114°, the eutectics between this compound and the picric acid and ether melting at 99° and 67·4°

respectively. *m*-Dinitrobenzene:dimethyl ether of quinol gives a single eutectic, m. p. about  $30^{\circ}$ , at a concentration of 50%. 2:4-Dinitrotoluene:dimethyl ether of quinol forms one eutectic, m. p. about  $30^{\circ}$ , at a concentration of 50%. 2:4:6-Trinitrotoluene (1 mol.) and the dimethyl ether of quinol (1 mol.) form a compound, m. p.  $43.3^{\circ}$ , the eutectics between this compound and the nitro-compound and ether melting at  $42.2^{\circ}$  and about  $38^{\circ}$  respectively. Picric acid (2 mols.) and the dimethyl ether of quinol (3 mols.) form a compound which has an indistinct melting point and dissociates on melting. *m*-Dinitrobenzene (1 mol.) and  $\beta$ -naphthol (1 mol.) give a compound, m. p. about  $62^{\circ}$  (dissociating). 2:4-Dinitrotoluene (1 mol.) and  $\beta$ -naphthol (1 mol.) form a compound, m. p.  $76.6^{\circ}$ , the eutectics between this compound and the components melting at about  $59^{\circ}$  and about  $74^{\circ}$  respectively. 2:4:6-Trinitrotoluene (1 mol.) and  $\beta$ -naphthol (1 mol.) give a compound, m. p.  $109.4^{\circ}$ , the eutectics between this compound and the components melting at  $73.5^{\circ}$  and  $97.5^{\circ}$  respectively.

The fused mixtures of the nitro-compounds examined with the ethers of  $\beta$ -naphthol and quinol and with  $\beta$ -naphthol are all more or less intense yellowish-red. Only for the systems in which a single eutectic appears are the mixtures pale yellow in the hot and almost colourless when cold.

T. H. P.

**4-Nitro-*o*-toluenesulphonic Acid.** S. V. HINTIKKA (Can. Pat. 200291).—This acid is prepared by sulphonating *p*-cymene to its *o*-sulphonic acid and treating the sulphonation mixture at  $40$ – $60^{\circ}$  with nitric and sulphuric acids; the isopropyl group is thus replaced by the nitro-group.

CHEMICAL ABSTRACTS.

**Condensation of Salicylaldehyde and Thymol. Synthesis of *o*-Hydroxyphenyldithymylmethane.** F. LAVILLA LLORENS (*Anal. Fis. Quim.*, 1920, **18**, 139–147).—The object of the investigation is to prepare triarylmethanes with a hydroxyl group on each benzene nucleus, and to study their physicochemical properties. The first of these compounds to be prepared is *o*-hydroxyphenyldithymylmethane,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_6\text{H}_2\text{MePr}^{\beta}\cdot\text{OH})_2$ , colourless, oblique prisms containing 1EtOH, m. p.  $185^{\circ}$ , from salicylaldehyde and thymol in presence of a small quantity of sulphuric acid. The *triacetyl* and *tribenzoyl* derivatives and the *trimethyl* and *triethyl* ethers are described; the last three compounds have m. p.  $126$ – $127^{\circ}$ ,  $137$ – $138^{\circ}$ , and  $77$ – $78^{\circ}$  respectively. A *tribromo*-derivative,  $\text{C}_{27}\text{H}_{29}\text{O}_3\text{Br}_3$ , m. p.  $170^{\circ}$ , is obtained in acetic acid solution. The corresponding *tri-iodo*-compound has m. p.  $111^{\circ}$ . The *trisodium* salt,  $\text{C}_{27}\text{H}_{29}\text{O}_3\text{Na}_3$ , crystals, is decomposed slightly by carbon dioxide. Amorphous precipitates are obtained: with lead salts, light yellow; copper salts, bluish-green; and ferric salts, yellowish-brown.

W. R. S.

**Molecular Compounds of Sulphur Dioxide with Amines.** A. KOREZYNSKI and M. GLEBOCKA (*Gazzetta*, 1920, **50**, i, 378–387).—The following compounds of sulphur dioxide with

amines have been prepared: with *p*-toluidine,  $C_7H_7 \cdot NH_2 \cdot SO_2$ , canary-yellow;  $\alpha$ -naphthylamine,  $C_{10}H_7 \cdot NH_2 \cdot SO_2$ , orange-yellow; *p*-chloroaniline,  $C_6H_4Cl \cdot NH_2 \cdot SO_2$ , canary-yellow; *p*-bromoaniline,  $C_6H_4Br \cdot NH_2 \cdot 0.5SO_2$  and  $C_6H_4Br \cdot NH_2 \cdot SO_2$ , canary-yellow; 3:5-dichloroaniline,  $C_6H_3Cl_2 \cdot NH_2 \cdot SO_2$ ; 2:4-dichloroaniline,

$C_6H_3Cl_2 \cdot NH_2 \cdot SO_2$ , canary-yellow; 3:5-dibromoaniline,  $C_6H_3Br_2 \cdot NH_2 \cdot SO_2$ , canary-yellow; *p*-nitrosodiethylaniline,  $C_8H_{10}O_2N_2 \cdot 2SO_2$ ; diphenylamine,  $C_{12}H_{11}N \cdot 0.5SO_2$ , orange;  $\alpha$ -naphthaquinoline, liquid compound;  $\gamma$ -chloroquinaldine,  $C_{10}H_8NCl \cdot 1.5SO_2$ ; aminoazobenzene,

$C_{12}H_{11}N_3 \cdot SO_2$ ; dimethylaminoazobenzene,  $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot NMe_2 \cdot 0.5SO_2$ ; dimethylaminoazobenzoic acid,  $CO_2H \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NMe_2 \cdot SO_2$ ; thiocarbamide,  $CH_4N_2S \cdot 0.5SO_2$ , colourless; ethyl *p*-aminobenzoate,

$C_8H_{11}O_2N \cdot 0.5SO_2$ , canary-yellow; *o*-aminocinnamic acid,  $C_9H_9O_2N \cdot SO_2$ , pale yellow; 2:4-tolylenediamine,  $C_7H_{10}N_2 \cdot SO_2$ , canary-yellow; *p*-nitro-*m*-phenylenediamine,  $C_6H_7O_2N_2 \cdot 0.5SO_2$ , yellow; benzidine,

$C_{12}H_{12}N_2 \cdot 2SO_2$ , canary-yellow; 1:3-diaminoazobenzene,  $C_{12}H_{12}N_4 \cdot 0.5SO_2$ ; tetramethyldiaminotriphenylmethane,  $C_{23}H_{26}N_2 \cdot 2.5SO_2$ ; leucaniline,  $C_{20}H_{21}N_3 \cdot 3SO_2$ , pale yellow; *p*-leucaniline,  $C_{19}H_{19}N_3 \cdot 1.5SO_2$ , pale yellow; rosaniline,  $C_{20}H_{21}ON_3 \cdot 1.5SO_2$ ; pararosaniline,

$C_{19}H_{19}ON_3 \cdot SO_2$ ; dimethylaminoacetanilide,  $C_{13}H_{17}ON_3 \cdot SO_2$ , canary-yellow; hexamethylenetetramine absorbs 36.6—37.8%  $SO_2$ , giving a colourless product of no definite molecular composition; caffeine,

$C_8H_{10}O_2N_4 \cdot 0.5SO_2$ , colourless; strychnine,  $C_{21}H_{29}O_5N_2 \cdot 2SO_2$ , pale yellow; brucine,  $C_{23}H_{26}O_4N_2 \cdot 3SO_2$ , yellow; morphine,  $C_{17}H_{19}O_3N \cdot 1.5SO_2$ , canary-yellow; quinine,  $C_{20}H_{24}O_2N_2 \cdot SO_2$ , lemon-yellow; papaverine,  $C_{20}H_{21}O_4N \cdot SO_2$ , straw-yellow; veratrine,  $C_{32}H_{49}O_6N \cdot 2.5SO_2$ , yellow; hæmatin,  $C_{32}H_{32}O_4N_4Fe \cdot 2.5SO_2$ ; atropine, cocaine, and narcotine form liquid additive compounds with sulphur dioxide, and no additive compounds are given by *o*-, *m*-, and *p*-nitroanilines, 2:4- and 3:5-dinitroanilines, trinitroaniline, 6-halogeno-2:4-dinitroanilines, *p*-nitrosoaniline, trihalogenated anilines, *m*- and *p*-nitrodimethylanilines, azobenzene, benzeneazonaphthyl ethyl ether, dimethylaminoazonitrobenzoic acid, carbamide, acetamide, benzamide, asparagine, thiocarbamide, acetanilide, acetophenetidide,  $\alpha$ -aminopropionic acid,  $\alpha$ -aminoisohexoic acid, aminobenzoic acids, sulphanic acid and its sodium salt, propyl *p*-aminobenzoate, *m*- and *p*-aminocinnamic acid, *o*-, *m*-, and *p*-aminophenols, *p*-chloro-*o*-aminophenol, ethyl *p*-amino-*m*-hydroxybenzoate, methyl *m*-amino-*p*-hydroxybenzoate, carbazole, *p*-benzoquinone, distyryl ketone, theobromine, and hæmin.

When kept in a desiccator, the above additive compounds lose sulphur dioxide; measurements of the pressures developed in this way are now being made.

The following general conclusions are drawn from the results obtained. Sulphur dioxide unites equally with primary, secondary,

and tertiary amines. Colourless amines containing an aromatic nucleus yield yellow additive compounds, whilst those free from such nucleus give colourless compounds. The appearance of the colour indicates the formation of secondary compounds, which are produced by virtue of the secondary valencies of the nitrogen atom. The action of such secondary valencies is diminished or entirely removed by the presence of negative substituents in the molecule, the influence of a nitro- or hydroxyl group being greater than that of a halogen atom. No direct dependence exists between the number of amino-groups and the number of molecules united with  $\text{SO}_2$ . In compounds of complicated structure, such as the alkaloids, the number of molecules united with  $\text{SO}_2$  is mostly greater than the number of nitrogen atoms.

When thoroughly dried reagents are used, carbon dioxide and hydrogen sulphide do not form additive compounds with *p*-toluidine,  $\alpha$ -naphthylamine,  $\alpha$ -naphthaquinoline, brucine, hæmin, or hæmatin. Similar failure to form compounds, even with ferrous sulphate and ferrous ammonium sulphate, is exhibited by nitric oxide.

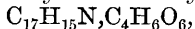
T. H. P.

**Syntheses of *s*-Xylidine.** HERBERT L. HALLER, ELLIOT Q. ADAMS, and EDGAR T. WHERRY (*J. Amer. Chem. Soc.*, 1920, **42**, 1840—1842).—*s*-Xylidine may be prepared from mesitylene by passage through mesitylenic acid and its amide, the latter being converted into the amine by Hofmann's reaction. A more satisfactory process is a modification of that of Willgerodt and Schmierer (A., 1905, i, 425), starting from *m*-4-xylidine. The authors find that, in this process, nitroacetylxylylide may be converted directly into nitroxylylene by heating the xylylide for fifteen minutes with sulphuric acid (D 1.84), pouring the product into a mixture of ethyl alcohol and sulphuric acid, diazotising with sodium nitrite, and distilling the product with steam in the presence of copper powder. *s*-Xylidine has m. p. 139.6—140.2°,  $n_D^{20}$  1.45,  $n_D^{169}$  1.69.

W. G.

**Separation of  $\alpha$ -Aminophenyl- $\alpha$ -naphthylmethane into its Optical Antipodes.** S. BERLINGOZZI (*Gazzetta*, 1920, **50**, ii, 56—59).—This compound, obtained as the racemic modification (this vol., i, 480), may be separated into its enantiomorphous components by fractional crystallisation of the tartrates from alcoholic solution.

*d*- $\alpha$ -Aminophenyl- $\alpha$ -naphthylmethane hydrogen tartrate,



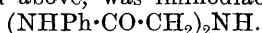
forms shining, white scales, m. p. 190—207° (decomp.). The free *d*-base,  $\text{C}_{17}\text{H}_{15}\text{N}$ , crystallises in white, translucent, triangular, or trapezoidal prisms, m. p. 81—82°,  $[\alpha]_D^{15} + 63.61^\circ$ . The *hydrochloride*,  $\text{C}_{17}\text{H}_{15}\text{N}, \text{HCl}$ , forms silky, white needles, m. p. 275—280° (decomp.),  $[\alpha]_D^{25} - 53.43^\circ$ .

*l*- $\alpha$ -Aminophenyl- $\alpha$ -naphthylmethane hydrogen tartrate forms tufts of white needles, m. p. 195—210° (decomp.). The free *l*-base crystallises in white, translucent, triangular prisms, m. p. 81—82°,  $[\alpha]_D^{15} - 63.38^\circ$ . The *hydrochloride* forms silky, white needles, m. p. 275—280°,  $[\alpha]_D^{25} + 53.18^\circ$ .

T. H. P.

**Amines. VIII. The Preparation of  $\omega$ -Aminoacetanilide.**

ARTHUR J. HILL and ERWIN B. KELSEY (*J. Amer. Chem. Soc.*, 1920, **42**, 1704—1711. Compare Dubsky and Granacher, A., 1918, i, 189).—To obtain a satisfactory yield of  $\omega$ -aminoacetanilide, the authors found it necessary to modify Majert's process (D.R.-P. 59121). The chloroacetanilide (550 grams) was added to 11 kilos. of 95% alcohol previously saturated with ammonia. The mixture was kept for five days at 20°, and then evaporated under diminished pressure to one-quarter of its volume. The liquid was poured into 3.5 litres of water, and the oil which separated was filtered after it had solidified. Aminoacetanilide was obtained from the filtrate by evaporating it nearly to dryness, and then recrystallising the residual material from water. The oil which separated and then solidified, as described above, was iminodiacetanilide,



In some preparations, a small amount of *nitrilotriacetanilide*,  $(\text{NHPh}\cdot\text{CO}\cdot\text{CH}_2)_3\text{N}$ , m. p. 238—239°, was isolated.

The authors were unable to obtain satisfactory yields of aminoacetanilide by Majert's process (D.R.-P. 59874) from aniline and ethyl aminoacetate hydrochloride.

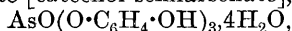
W. G.

**Preparation of "Cupferron."** D. R. KASANOF (*J. Ind. Eng. Chem.*, 1920, **12**, 799).—The yield of the intermediate substance, phenylhydroxylamine, in the preparation of "cupferron" (A., 1911, ii, 939) depends on the quality of the zinc dust used to reduce the nitrobenzene, but consistently good yields may be obtained if the zinc dust is previously treated with 2% mercurous nitrate solution slightly acidified with nitric acid.

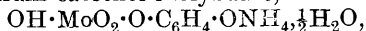
W. P. S.

**Crystallographic Properties of some Catechol Derivatives of Acids of Heavy Metals and their Salts.** P. J. BEGER (*Centr. Min.*, 1920, 129—142).—The compounds, the crystallographic properties of which are described in considerable detail, were prepared by Weinland and his collaborators (A., 1919, i, 442).

Tricatechol arsenate [catechol semiarsenate],



small, shining, colourless crystals of cubic habit, belonging to the rhombic, bipyramidal system,  $a:b:c=0.958:1:0.988$ . There are perfect cleavages parallel to the three pinacoid faces. Optic axial plane,  $\{010\}$ . The chromium salt,  $[\text{AsO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O})_3]_3\text{H}_6\text{Cr}\cdot 12\text{H}_2\text{O}$ , the cobalt salt,  $[\text{AsO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O})_3]_2\text{H}_4\text{Co}\cdot 8\text{H}_2\text{O}$ , and the corresponding nickel salt, all crystallise in the cubic system. The sodium salt of the nickel derivative,  $\text{Ni}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{ONa})_2\cdot 12\text{H}_2\text{O}$ , forms greenish-black, monoclinic, prismatic crystals, the axial ratios of which could not be completely determined;  $a:b:c=1.19:1:?$ ;  $\beta=102.5^\circ$  approx. Ammonium catechol molybdate,



forms reddish-black prisms, rhombic bipyramidal,  $a:b:c=0.5890:1:0.9105$ . The crystals, which sometimes show vicinal faces with complex indices, cleave perfectly parallel to  $\{010\}$  and  $\{001\}$ .

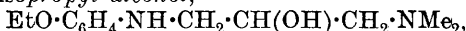
E. H. R.

**Quinol.** J. MESSNER (*Pharm. Zentr.-h.*, 1920, **61**, 454—455).—The statement found generally in literature that quinol reduces Fehling's solution in the cold and silver nitrate only when heated is incorrect. Quinol reduces silver nitrate at the ordinary temperature, with the separation of metallic silver; it at once changes the colour of Fehling's solution to green, but a precipitate of cuprous oxide forms only after long contact or when the mixture is heated. The reactions are therefore of little use for distinguishing quinol from catechol.

W. P. S.

**Amino-alcohols Derived from  $\alpha$ -Anilino- $\gamma$ -dialkylaminoisopropyl Alcohols.** E. FOURNEAU and J. RANEDO (*Anal. Fis. Quim.*, 1920, **18**, 133—139).—The physiological effect of the replacement of a phenoxy- by an anilino-group in amino-alcohols derived from aniline and its homologues was investigated. The aromatic amine was made to react with epichlorohydrin, and the derivative thus obtained treated with dimethylamine or one of its homologues.

The following substances are described:  $\alpha$ -p-phenetidino- $\gamma$ -dimethylaminoisopropyl alcohol,



b. p.  $212^\circ/14$  mm., m. p.  $79^\circ$ ;  $\alpha$ -p-toluidino- $\gamma$ -dimethylaminoisopropyl alcohol,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{NMe}_2$ , b. p.  $190^\circ/12$  mm., m. p.  $72^\circ$ ;  $\alpha$ -methylanilino- $\gamma$ -dimethylaminoisopropyl alcohol,  $\text{NMePh} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{NMe}_2$ , b. p.  $168^\circ/14$  mm.;  $\alpha$ -anilino- $\gamma$ -dimethylaminoisopropyl alcohol, b. p.  $195^\circ/21$  mm., m. p.  $84^\circ$ ;  $\alpha$ -ethylanilino- $\gamma$ -dimethylaminoisopropyl alcohol, b. p.  $195^\circ/15$  mm.;  $\alpha$ -m-nitroanilino- $\gamma$ -dimethylaminoisopropyl alcohol, m. p.  $95^\circ$ ; and  $\alpha$ -o-anisidino- $\gamma$ -dimethylaminoisopropyl alcohol, b. p.  $198$ — $200^\circ/30$  mm.

The anæsthetic action of benzoylmethylanilinoisopropyl alcohol hydrochloride is slower than that of stovaine; total anæsthesia is obtained in twenty minutes with  $N/50$ -solutions, and in seventeen minutes with  $N/25$ -solutions;  $N/25$ -stovaine solutions, on the other hand, act in four to five minutes.

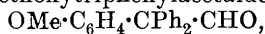
W. R. S.

**The Hydrobenzoin Transposition. Influence of the Nature of the Reagent.** M. TIFFENEAU and A. ORÉKHOFF (*Compt. rend.*, 1920, **171**, 400—402. Compare Tiffeneau and Dorlencourt, A., 1906, i, 724; Orékhoff, A., 1919, i, 272).—With the exception of  $\alpha\beta\beta$ -triphenylethanediol, which is really an aryl hydrobenzoin, the dehydration of the alkylhydrobenzoins may take place in several different ways, depending on the concentration of the sulphuric acid used and the nature of the alkyl group.

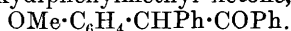
Thus, with dilute sulphuric acid,  $\alpha\beta$ -diphenylbutane- $\alpha\beta$ -diol yields  $\alpha\alpha$ -diphenylbutaldehyde, but with concentrated sulphuric acid it gives ethyldeoxybenzoin and diphenylmethyl ethyl ketone.  $\alpha\beta$ -Diphenylpropane- $\alpha\beta$ -diol, on the other hand, only yields methyldeoxybenzoin with concentrated sulphuric acid.

W. G.

**The Hydrobenzoin Transposition. Influence of the *p*-Methoxyl Substitution on the Dehydration of Triarylethanediols.** A. ORÉKHOFF and M. TIFFENEAU (*Compt. rend.*, 1920, 171, 473—476).—Under the influence of the same dehydrating agent, the triarylethanediols undergo change with or without molecular transposition. When the secondary alcohol group is attached to the same carbon atom as a phenyl group, there is no transposition, a ketone being formed. If the phenyl group is replaced by an anisyl group, there is transposition, with the formation sometimes of a single compound, a triarylacetaldehyde, the anisyl group migrating, sometimes with the formation of two compounds, the aldehyde and a ketone, in which case the phenyl group migrates. These reactions, simple and mixed, depend on the position of the hydroxyl group eliminated, and the stability of the hydroxyl groups appears to depend on the nature of the substituent groups. Thus  $\alpha\beta$ -dianisyl- $\alpha$ -phenylethanediol yields *pp'*-dimethoxytriphenylacetaldehyde,  $(\text{C}_6\text{H}_4\cdot\text{OMe})_2\text{CPh}\cdot\text{CHO}$ , whilst  $\alpha\alpha$ -diphenyl- $\beta$ -anisylethanediol yields *p*-methoxytriphenylacetaldehyde,



and phenyl *p*-methoxydiphenylmethyl ketone,



W. G.

**Preparation of Mercury Compounds of Sulphophenolcarboxylic Acids and their Homologues which yield Colloidal Solutions with Water.** SACCHARIN-FABRIK AKTIENGESELLSCHAFT VORM. FAHLBERG LIST & Co. (D.R.-P. 321700; from *Chem. Zentr.*, 1920, iv, 292).—(i) The mercuration of the sulphocarboxylic acids is effected in acid solution. (ii) The solutions of sulphophenolcarboxylic acids or their homologues are warmed or allowed to remain in contact with solutions of mercury salts, or the aqueous solutions of the sulphocarboxylic acids are similarly treated with an amount of mercuric oxide insufficient for the saturation of the three acidic groups (less than 1.5 molecules of oxide for each molecule of sulphophenolcarboxylic acid). Alternatively, the mercury compounds of the sulphophenolcarboxylic acids, which are sparingly soluble or insoluble in water, are warmed with acids or mixtures or compounds containing mercury and salicylic acid, or its homologues are treated at the ordinary or elevated temperature with concentrated sulphuric acid, and subsequently with a dilute acid. *Mercurisulphosalicylic acid* (from 5-sulphosalicylic acid) and *mercurisulpho-m-cresotic acid* form colourless crystals, very sparingly soluble in organic media, readily soluble in water to colloidal, viscous solutions.

H. W.

**Reduction of *o*-Benzoicsulphinide ["Saccharin"].** F. GIANFORMAGGIO (*Gazzetta*, 1920, 50, i, 327—340).—Previous investigations on reduction by means of amyl alcohol and sodium have been confined more especially to *o*-phenolcarboxylic acids, with which the benzene nucleus undergoes rupture between the hydroxyl and carboxyl groups, acids of the pimelic acid series being produced, and to *m*-phenolcarboxylic and *o*- and *p*-amino-



benzoic acids, which are reduced without rupture of the benzene ring.

In the reduction of *o*-benzoisulphinide by means of sodium and amyl alcohol, the nascent hydrogen formed eliminates the imino-group as ammonia, and also detaches the sulphonic group, which, after acidification, is liberated as sulphur dioxide; the final product of the reaction is hexahydrobenzoic acid, *o*-sulphobenzoic acid being probably formed as an intermediate product.

Of the various secondary products formed in reductions by means of sodium and amyl alcohol, owing to reactions between the alcohol and its sodium derivative (compare Einhorn and Lumsden, A., 1896, i, 45; Guerbet, A., 1899, i, 472), the author has identified only valeric acid.

A basic compound, which distils in a current of steam, is also formed in small proportion during the reduction of *o*-benzoisulphinide, and is to be investigated further. T. H. P.

#### Action of Acetic Anhydride on $\alpha$ -Naphthylpropionic Acid.

BYRON L. WEST (*J. Amer. Chem. Soc.*, 1920, **42**, 1656—1669).—When heated with potassium cyanide, sodium naphthalene- $\alpha$ -sulphonate gave  $\alpha$ -naphthonitrile, from which  $\alpha$ -naphthoamide was prepared. The latter, when reduced in alcoholic hydrochloric acid with sodium amalgam, gave  $\alpha$ -naphthylmethyl alcohol, which was readily oxidised to  $\alpha$ -naphthaldehyde. This aldehyde, when treated with malonic acid in the presence of alcoholic ammonia and subsequent addition of acid, gave a mixture of two acids, which, on heating, yielded  *$\alpha$ -naphthylacrylic acid*, m. p. 207·5°, giving an *ethyl* ester. On bromination, the ester gave *ethyl  $\alpha\beta$ -dibromo- $\beta$ -1-naphthylpropionate*,  $C_{10}H_7\cdot CHBr\cdot CHBr\cdot CO_2Et$ , which, with alcoholic potassium hydroxide, yielded  *$\alpha$ -naphthylpropionic acid*,  $C_{10}H_7\cdot C:C\cdot CO_2H$ , m. p. 134—135°, giving a *potassium* salt.

When heated with acetic anhydride,  $\alpha$ -naphthylpropionic acid yielded *8- $\alpha$ -naphthylphenanthrene-6:7-dicarboxylic anhydride*, m. p. 207—209° (compare Michael and Bucher, A., 1898, i, 256), from which a very insoluble *sodium* salt was prepared. The anhydride gave Baeyer's phthalein reaction and fluorescein test. W. G.

#### Preparation and Properties of Cellulose Phthalate. H. A.

LEVY (*J. Ind. Eng. Chem.*, 1920, **12**, 743—744).—Cellulose phthalate,  $C_8H_4O_3\cdot 8C_6H_{10}O_5\cdot 4H_2O$ , was prepared by heating cotton cellulose (previously converted into "hydrocellulose" by treatment with a solution of chlorine in glacial acetic acid) for twenty-four hours at 70° with phthalic anhydride and zinc chloride in the minimum quantity of ethyl phthalate (or acetic acid), washing the resulting ester, and drying it not above 70° in a vacuum. The cellulose phthalate thus obtained was insoluble in alcohol, ether, acetic acid, ethyl phthalate, and other ordinary solvents. The presence of zinc chloride or other condensing agent is essential for the esterification. Phthalic anhydride does not displace the acetate radicle from cellulose acetate or the nitrate radicle from cellulose nitrate, even when the zinc chloride is replaced by sulphuric acid.

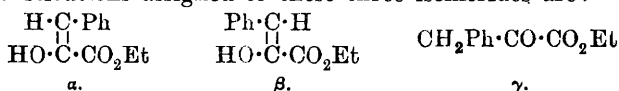
C. A. M.

**Catalytic Hydrogenation of Cholesterol and Cholesterylene.** F. F. NORD (*Biochem. Zeitsch.*, 1919, 99, 261—267).—Cholesterol in acetone solution was reduced by hydrogen in the presence of colloidal palladium until no more of the gas was absorbed. The dihydrocholesterol,  $C_{27}H_{48}O$ , produced, m. p.  $141^{\circ}$ , formed an acetyl derivative, m. p.  $110^{\circ}$ . Cholesterylene was hydrogenised in the same way, and yielded cholestane, b. p.  $269\text{—}271^{\circ}/12\text{ mm.}$ ,  $[\alpha]_D^{25} + 43.32^{\circ}$ . S. S. Z.

**Action of Alcoholic Sodium Acetate Solution on Cholesterol Dibromide.** A. WINDAUS and H. LÜDERS (*Zeitsch. physiol. Chem.*, 1920, 109, 183—185).—The authors have prepared the so-called metacholesterol described by Lifschütz (A., 1919, i, 591), and find that: (1) it yields ordinary cholesterol dibromide, reduction of which gives cholesterol, m. p.  $146^{\circ}$ ; (2) its melting point is raised from  $141\text{—}142^{\circ}$  to  $145^{\circ}$  by repeated crystallisation from methyl alcohol; (3) the isobutyrate and acetate are identical with those prepared from cholesterol. The conclusion is drawn that "metacholesterol" consists principally of ordinary cholesterol.

T. H. P.

**Isomerism in the Series of Aromatic  $\alpha$ -Ketonic Acids.** H. GAULT and R. WEICK (*Compt. rend.*, 1920, 171, 395—398).—It has previously been shown (this vol., i, 485) that ethyl phenylpyruvate can be obtained in two isomeric forms,  $\alpha$ -, m. p.  $51^{\circ}$ , and  $\beta$ -, b. p.  $149^{\circ}/15\text{ mm.}$  A third isomeride,  $\gamma$ -, m. p.  $79^{\circ}$ , has now been obtained by the action of sodium acetate on the  $\beta$ -isomeride. The constitutions assigned to these three isomerides are:



It is shown that the  $\alpha$ - and  $\beta$ -isomerides, when brominated in carbon disulphide solution at  $-15^{\circ}$ , give a *dibromo*-derivative,  $\text{CHPhBr}\cdot\text{CBr}(\text{OH})\cdot\text{CO}_2\text{Et}$ , m. p.  $55\text{—}60^{\circ}$ , which decomposes very rapidly at the ordinary temperature, losing hydrogen bromide and giving the *compound*,  $\text{CHPhBr}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ , b. p.  $184^{\circ}/20\text{ mm.}$  The  $\gamma$ -isomeride is only brominated in boiling carbon disulphide, and gives *ethyl  $\beta$ -bromo- $\alpha$ -keto- $\beta$ -phenyl- $\gamma$ -benzylbutyrolactone- $\gamma$ -carboxylate*,  $\text{CO}\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}(\text{CO}_2\text{Et})\cdot\text{CH}_2\text{Ph} \\ \diagdown \quad \diagup \\ \text{CO}\cdot\text{CPhBr} \end{array}$ , m. p.  $151^{\circ}$ .

The  $\alpha$ - and  $\gamma$ -esters are converted into the  $\beta$ -ester by slow distillation under reduced pressure. The  $\beta$ - and  $\gamma$ -esters are converted into the  $\alpha$ -ester by shaking in ethereal solution with sodium carbonate, whilst the  $\beta$ -ester is converted into the  $\gamma$ -ester, as described above. W. G.

**Preparation of Aldehydes and Ketones.** CARL HARRIES (D.R.P. 321567; from *Chem. Zentr.*, 1920, iv, 292).—Ozonides are treated with reducing agents, particularly with potassium ferrocyanide, in the presence or absence of acids, whereby the formation of resins is considerably restricted. The solution of *isoeugenol* ozonide in ethyl acetate gives *vanillin* in 95% yield.

*n*-Oleic acid ozonide gives nonaldehyde. The ozonides from tar oil, gas oil, and the unsaturated oils, obtained by chlorination of crude paraffin and elimination of hydrogen chloride, yield mainly aldehydes in addition to ketones and small amounts of acids.

H. W.

**Manufacture of Protocatechualdehyde.** CONFECTIONERY INGREDIENTS, LTD., FRANCIS EDWARD MATTHEWS, ALBERT THEODORE KING, and THOMAS KANE (Brit. Pat. 145871).—The acid chloride of any suitable acyl derivative of protocatechuic acid, such as the diacetate, dibenzoate, carbonate, or di-*p*-toluenesulphonate, or of the dibenzyl ether of protocatechuic acid, is reduced to the corresponding derivative of protocatechualdehyde by treatment in an inert solvent at boiling temperature with hydrogen in presence of a hydrogenating catalyst, such as palladium or nickel. When the evolution of hydrogen chloride ceases, the reduction product is hydrolysed and protocatechualdehyde isolated as its bisulphite compound in the usual way.

G. F. M.

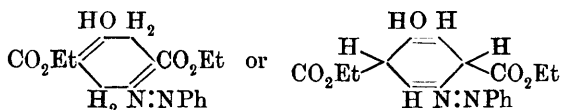
**Perfumes from Perillaldehyde.** S. FURUKAWA (Jap. Pat. 35332).—An alcoholic solution of the aldehyde (150 grams in 500 c.c.) is heated for two hours on the water-bath with hydroxylamine hydrochloride (70 grams) and sodium hydrogen carbonate (100 grams). The resulting oxime, m. p. 102°, is two thousand times as sweet as sucrose; it is easily converted into perillonitrile, b. p. 116–118°/11 mm.,  $D^{15}_D$  0.94–0.949, which is two hundred times as sweet as sucrose, and is suitable as an ingredient of tooth-powders or perfumes.

CHEMICAL ABSTRACTS.

**The Isomerism of the Oximes. IX. 2:4-Dinitrobenzaloxime and Bromo-substituted Hydroxy- and Methoxybenzaloximes.** VERA WENTWORTH and OSCAR LISLE BRADY (T., 1920, 117, 1040–1045).

**Unsaturated Compounds in Organic Chemistry. II. Constitution of Succinylsuccinic Ester.** M. GIUA (*Gazzetta*, 1920, 50, i, 387–393).—The action of phenylhydrazine and of *o*s-phenylmethylhydrazine on ethyl succinylsuccinate has been investigated (compare Knorr and Bülow, A., 1884, 1380; von Baeyer, Jay, and Jackson, A., 1891, 1486; von Baeyer and von Brüning, A., 1891, 1486; Kijner, A., 1894, i, 67).

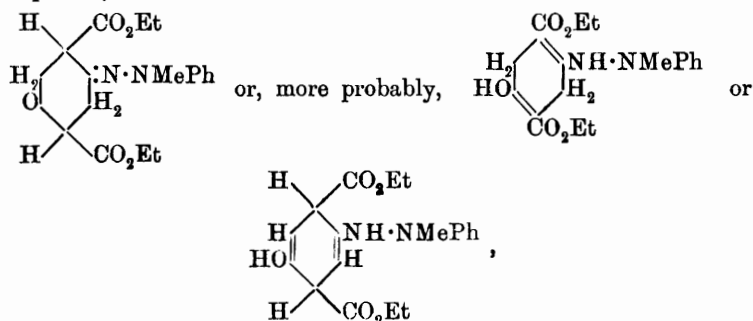
The action of phenylhydrazine (1 mol.) on ethyl succinylsuccinate (1 mol.) in alcoholic solution and in presence of acetic acid yields (1), as principal product, the compound,



which crystallises in carmine-red, prismatic needles, m. p. 142°, dissolves in sulphuric acid to a colourless solution, and is only slowly attacked by boiling concentrated alkali solution. Reduction of this compound by means of sodium and alcohol yields a violet

compound, which does not melt at  $240^{\circ}$  and dissolves in alkali solution with yellow coloration. (2) Ethyl benzenedihydrazodihydroterephthalate, m. p.  $204-205^{\circ}$  (compare Knorr, *loc. cit.*; von Baeyer, *loc. cit.*). The latter and its isomeride, m. p.  $166^{\circ}$ , form the principal products of the reaction when 2 mols. of phenylhydrazine are taken per 1 mol. of the succinylsuccinic ester. Whatever the proportions between the reacting compounds, the reaction yields always a viscous, tar-like resin, which partly decomposes, with formation of aniline, when distilled under a pressure of 52 mm.

The action of *as*-phenylmethylhydrazine on ethyl succinylsuccinate in alcoholic solution containing acetic acid yields the compound,



which crystallises in golden-yellow needles, m. p.  $135-136^{\circ}$ , and dissolves in concentrated sulphuric acid, giving a reddish-yellow solution. T. H. P.

**Manufacture of Aromatic Alkylamino-compounds [Alkyl-aminoanthraquinones].** FREDERICK WILLIAM ATTACK and WALTER NORMAN HAWORTH (Brit. Pat. 147964).—The aminoanthraquinones are alkylated by treatment with an alkyl sulphate in solution in a neutral medium of high boiling point, such as nitrobenzene or tetrachloroethane, in presence of a mild alkali, such as sodium carbonate. Thus 20 parts of 1-aminoanthraquinone may be dissolved in 216 parts of nitrobenzene and 20 parts of sodium carbonate added, the mixture being heated to boiling under a reflux condenser, while  $17\frac{1}{2}$  parts of methyl sulphate are added during the space of two hours. A yield of 87% of 1-methylaminoanthraquinone is obtained. When 5 parts of 2-aminoanthraquinone are similarly treated with 6 parts of methyl sulphate, 2-dimethylaminoanthraquinone is the chief product. G. F. M.

**Rhinanthocyanin.** A. NESTLER (*Ber. deut. bot. Ges.*, 1920, 38, 117—121).—When rhinanthin is extracted from the seeds of *Alectorolophus hirsutus* by means of 70% alcohol containing 5% of hydrochloric acid, the glucoside is gradually hydrolysed by the acid into a blue colouring matter, rhinanthocyanin, and a sugar. This hydrolysis may be effected also, although less rapidly, by sulphuric,

oxalic, citric, lactic, or acetic acid, and the production of the so-called blue (mostly dark brownish-violet) bread is due to contamination of the flour with the meal of seeds containing rhinanthin and hydrolysis of the latter by means of the lactic acid formed during the fermentation. In the course of a few hours or days, the blue rhinanthocyanin solution becomes colourless and deposits blue or green granules, which sometimes retain their colour for many weeks, and sometimes turn brown. Rhinanthocyanin imparts a blue or green coloration to chloroform, but does not dissolve therein; the colour is due to the presence of granules,  $0.7\text{--}1\ \mu$  in size, and of droplets of  $2.5\text{--}7\ \mu$ , and is removable by ultra-filtration.

T. H. P.

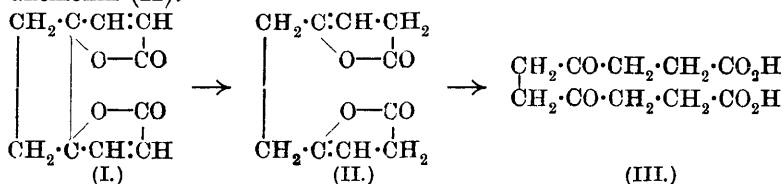
### Chitin and Chitin Derivatives of Animal and Plant Origin.

O. SCHMIEDEBERG (*Arch. expt. Path. Pharm.*, 1920, **87**, 74—86).—Chitin was prepared by dissolving moulds, previously freed from cellulose, in concentrated hydrochloric acid and filtering; the chitin was then precipitated from the filtrate by the addition of water and washed until free from chloride. From the elementary analysis, the formula  $\text{C}_{34}\text{H}_{56}\text{O}_{22}\text{N}_4$  was calculated, which suggests that the chitin lost one acetyl group in the treatment with hydrochloric acid. It seems to resemble chitin of animal origin, with the exception that it is less resistant to the action of acids and alkalis. A compound resembling Winterstein's paradextran was prepared by the author from mould cellulose. The work of previous investigators on chitin is reviewed.

S. S. Z.

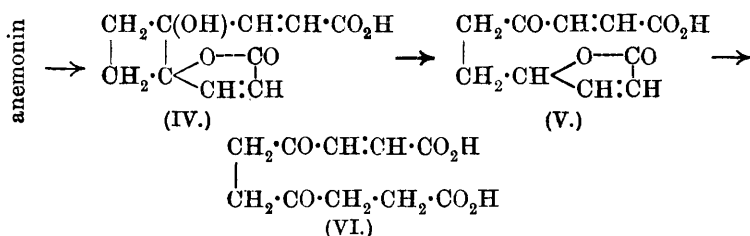
### Transformations of Anemonin by Acids and Alkalis. VI.

Y. ASAHINA and A. FUJITA (*J. Pharm. Soc. Japan*, 1920, No. 461. Compare A., 1892, i, 241; 1896, i, 623; 1899, i, 930; 1914, i, 561; 1915, i, 1067; 1916, i, 401; this vol., i, 70, 321, 493).—Having settled the constitution of anemonin (I) by synthesis (this vol., i, 493), the authors now explain its transformations. Cold sulphuric acid is without action; the hot, dilute acid changes it to anemoninic acid (VI). Cold concentrated hydriodic acid dissolves the substance, and, on keeping, anemonolic acid (III) separates quantitatively, probably after intermediate formation of dihydro-anemonin (II).

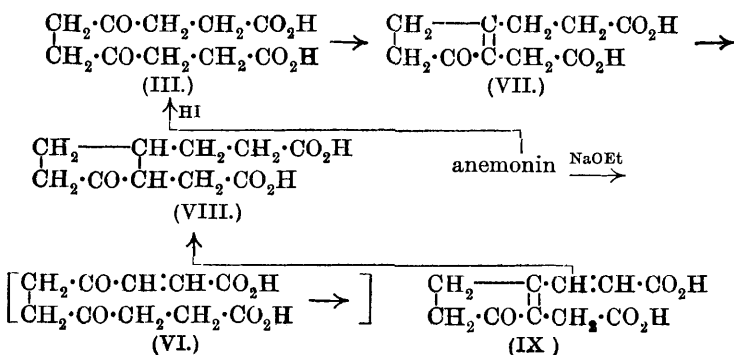


When warmed with methylsulphuric acid, anemonin yields the *methyl ester*,  $\text{C}_{12}\text{H}_{14}\text{O}_5$ , m. p.  $62^\circ$ , of furan-2-propionic-5-acrylic acid, m. p.  $179^\circ$ . This acid is reduced by sodium amalgam to furan-2:5-dipropionic acid, which is also formed by prolonged heating of anemonolic acid above its melting point. The authors cannot confirm the higher melting point of furan-2-propionic-5-acrylic acid given by Cooper and Nuttall (T., 1914, **105**, 2218).

Concentrated potassium carbonate solution changes anemonin into anemoninic acid (VI), which can be isolated in a 10% yield as crystals of the  $\alpha$ -variety, m. p.  $117^{\circ}$ . This is readily transformed by concentrated hydrochloric acid at  $60^{\circ}$  to the  $\beta$ -variety, m. p.  $189^{\circ}$ . The two forms are probably *cis-trans*-modifications. Both yield with ammonia an impure pyrrole derivative. The  $\beta$ -acid yields with concentrated sulphuric acid and methyl alcohol its own methyl ester, m. p.  $128^{\circ}$ , together with that of furan-2-propionic-5-acrylic acid (above). Anemoninic acid is oxidised by permanganate to acetonediacetic ( $\gamma$ -ketopimelic) acid. The formation of anemoninic acid (VI) from anemonin is represented as follows; IV and V are hypothetical:



Sodium and 98% alcohol transform anemonin into  $\alpha$ -anemononic acid (IX), m. p.  $120^{\circ}$ , which is changed by heating with concentrated hydrochloric acid to the stereoisomeric  $\beta$ -variety, m. p.  $210^{\circ}$ . Both are reduced catalytically to the same tetrahydroanemononic acid (VIII), m. p.  $135^{\circ}$ . Anemononic acid (III) is transformed by alcoholic potassium hydroxide at the ordinary temperature to *anhydroanemononic acid* (VII),  $\text{C}_{10}\text{H}_{12}\text{O}_5$ , m. p.  $129^{\circ}$ , yielding a *semicarbazone*, m. p.  $208^{\circ}$ . This acid combines with one molecule of hydrogen catalytically, and is then found to be identical with tetrahydroanemononic acid (VIII), formed by reduction of anemononic acid, whence the constitution IX is deduced for the latter. Its formation from anemonin by sodium ethoxide is attributed to the intermediate formation of anemoninic acid (VI), although the latter itself could not be converted into anemononic acid.



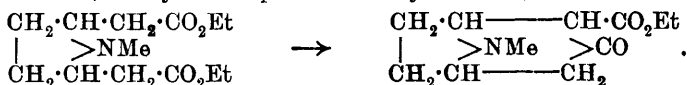
**Nature of the Red Dye of Crustaceæ.** J. VERNE (*Compt. rend. Soc. Biol.*, 1920, **83**, 963—964; from *Chem. Zentr.*, 1920, iii, 259).—The red dye of crustaceæ behaves in the same manner as carotin towards solvents. The latter also yields a violet-brown additive compound with iodine and a blue coloration with sulphuric acid. The absorption bands of both dyes are similar. The dye of the crustaceæ is a compound with carbon and hydrogen in the ratio 5:7, and, according to ebullioscopic determinations, has the empirical formula  $C_{40}H_{56}$ . H. W.

**A Comparative Study in the Xanthone Series. I.** SURENDRA NATH DHAR (T., 1920, **117**, 1053—1070).

**Preparation of Derivatives of Hydrastinine.** KARL W. ROSENMUND (D.R.-P. 320480; from *Chem. Zentr.*, 1920, iv, 223).—The process depends on (i) the treatment of methylenedioxyphenylisopropylamine with formaldehyde or substances which yield formaldehyde and catalytically active agents, and oxidation of the condensation product thus formed; (ii) the condensation of methylenedioxyphenylisopropylamine with formaldehyde or substances which yield formaldehyde, transformation of the alkylideneamine thus produced with the aid of active catalysts, alkylation, and oxidation of the substance so formed; (iii) the use of iodine as oxidising agent. 6:7-Methylenedioxy-3-methyltetrahydroisoquinoline, m. p. 65—67°, is obtained by heating the oily product of the action of calculated quantities of methylenedioxyphenylisopropylamine and formaldehyde with hydrochloric acid (25%) at 100°. The base is converted by methyl iodide into 3-methyldihydrohydrastinine hydriodide, m. p. 240°; the free base has m. p. 86°, whilst the hydrochloride has m. p. 230°. The hydrochloride is directly obtained when methylenedioxyphenylisopropylamine hydrochloride (1 part) and commercial formaldehyde solution (2 parts) are heated for three hours at 130—135°. 3-Methyldihydrohydrastinine is converted by iodine and potassium acetate in alcoholic solution into 3-methylhydrastinine hydriodide, m. p. 207° (base, m. p. 103—104°). The dichromate, obtained by the action of potassium dichromate and sulphuric acid on an aqueous solution of 3-methyldihydrohydrastinine hydrochloride, is oily. 3-Methyl-N-ethylhydrastinine hydriodide separates on boiling a solution of 3-methyldihydronorhydrastinine in benzene, and is oxidised to 3-methyl-N-ethylnorhydrastinine (hydriodide, yellow crystals, m. p. 210°). The products are less toxic than hydrastinine. H. W.

**Preparation of Tropinonecarboxylic Esters.** R. WILLSTÄTTER (D.R.-P. 302401; from *Chem. Zentr.*, 1920, iv, 42—43).—N-Methylpyrrolidinediacetic esters are treated with an alkali metal or other condensing agent. The initial material for the synthesis is succinyldiacetic ester, which is transformed by methylamine in

acetic acid solution, for example, into the corresponding *N*-methylpyrrolediacetic ester; the latter is reduced by hydrogen in the presence of platinum in acetic acid solution to *N*-methylpyrrolidinediacetic ester. The diethyl ester is a colourless, mobile oil with an alkaline reaction, b. p. 162·5°/9 mm., whilst the methyl ester has b. p. 155·5°/12 mm. The *N*-methylpyrrolidinediacetic esters lose alcohol under the influence of sodium, sodium alkoxides, or sodamide, and yield tropinonecarboxylic esters,



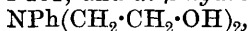
For further preparations, the ester is only obtained in solution or mixed with sodium salts; its separation from admixture with organic substances is difficult, since it is very readily decomposed and resinified; it is very slightly soluble in water and exhibits a strong ferric chloride reaction. Ethyl tropinonecarboxylate is converted by warm dilute acid into tropinone, which can be isolated in substance or as the picrate or dibenzylidene derivative; it is reduced electrolytically or by sodium amalgam to *r*-ecgonine ester.

H. W.

#### Heterocyclic Compounds of *N*-Arylamino-alcohols. R. E.

RINFUSZ and V. L. HARNACK (*J. Amer. Chem. Soc.*, 1920, **42**, 1720—1725).—Aniline condenses with trimethylene chlorohydrin to give *γ*-hydroxypropylaniline,  $\text{NPh} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , b. p. 192°/30 mm.,  $n_D^{20}$  1·502,  $D_4^{25}$  1·063, and *di-γ*-hydroxypropylaniline,  $\text{NPh}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH})_2$ , b. p. 241—242°/25 mm.,  $n_D^{24}$  1·565,  $D_4^{26}$  1·097. When dehydrated by phosphoric oxide, the first-named compound yields tetrahydroquinoline, whilst the second yields julolidine. Tetrahydroquinoline, when condensed with allyl bromide, gives 1-allyltetrahydroquinoline, b. p. 135°/25 mm.,  $n_D^{24}$  1·556,  $D_4^{24}$  1·024, and with trimethylene chlorohydrin gives 1-*γ*-hydroxypropyltetrahydroquinoline, b. p. 227—229°/18 mm.,  $n_D^{31}$  1·561,  $D_4^{27}$  1·091, which, on dehydration, yields julolidine.

*β*-Hydroxyethylaniline,  $\text{NPh} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , has b. p. 188°/30 mm.,  $n_D^{24}$  1·576,  $D_4^{24}$  1·101, and *di-β*-hydroxyethylaniline,



has b. p. 228°/15 mm., m. p. 53·5—54°. *β*-Hydroxyethylaniline on dehydration gives diphenylpiperazine, and di-*β*-hydroxyethylaniline yields phenylmorpholin.

W. G.

**The Cyanine Dyes. II. The Synthesis of *o*-Amino-cinnamylidenequinaldine Methiodide.** WILLIAM HOBSON MILLS and PERCY EDWIN EVANS (*T.*, 1920, **117**, 1035—1040).

**Thiocyanates and Thiocarbimides. XIV. A New Method of Synthesising 2-Thiohydantoins.** TREAT B. JOHNSON, ARTHUR J. HILL, and ERWIN B. KELSEY (*J. Amer. Chem. Soc.*, 1920, **42**, 1711—1720).—*ω*-Aminoacetanilide reacted with carbon disulphide



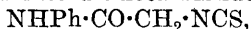
in alcoholic solution to give the unstable *ω*-aminoacetanilide salt of the corresponding dithiocarbamic acid,

$\text{NHPh}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CS}\cdot\text{SH}, \text{NH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$ ,  
m. p.  $145^\circ$  (decomp.), which, by the action of ethyl chloroformate, was converted into the *carbethoxy*-derivative,

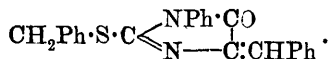
$\text{NHPh}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CS}\cdot\text{S}\cdot\text{CO}_2\text{Et}$ ,  
and this, on distillation, yielded 2-thio-1-phenylhydantoin. This thiohydantoin, when digested with chloroacetic acid, was converted into 1-phenylhydantoin.

When ethyl chloroformate acted directly on *ω*-aminoacetanilide, *ω*-carbethoxyaminoacetanilide, m. p.  $137.5^\circ$ , was obtained, which was converted by the action of alcoholic potassium hydroxide into 1-phenylhydantoin.

The dithiocarbamate (above), when digested with mercuric chloride, was converted into *ω*-thiocarbimidoacetanilide,

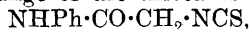


which spontaneously and immediately condensed to give 2-thio-1-phenylhydantoin, the benzylidene derivative of which condensed with benzyl chloride in the presence of sodium ethoxide to give 2-benzylthiol-1-phenyl-4-benzylidenethydhantoin,



m. p.  $178^\circ$ .

The spontaneous change of the thiocarbimide,



into 2-thio-1-phenylhydantoin, and the series of changes described above, are taken as strong support of the view that the conversion of compounds of the type  $\text{NHR}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$  into *ψ*-thiohydantoin, is by passage through the normal thiocyanate (A., 1918, i, 256), and not through the thiocarbimide (Beckurts and Frerichs, A., 1915, i, 798, 799).

W. G.

### Preparation of Isatin and its Substitution Products.

J. R. GEIGY (D.R.-P. 320647; from *Chem. Zentr.*, 1920, iv, 223).—*ω*-Oximinoacetanilide,  $\text{NHPh}\cdot\text{CO}\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ , or its halogen, alkyl, alkyl, or carboxyl substitution products, which are capable of condensation, are warmed with concentrated sulphuric acid, and the isatinimines, of the general formula  $\text{R}\begin{array}{c} \nwarrow \text{NR}' \\ \nearrow \text{C}(\text{NH}) \end{array}\text{CO}$  (in which R represents a substituted or unsubstituted benzene nucleus and R' a hydrogen, alkyl, or arylalkyl group), which are thus formed are decomposed by water into isatins and ammonia. The following examples are cited: isatin from *ω*-oximinoacetanilide; 5-methylisatin from *ω*-oximinoaceto-*p*-toluidide; 4-chloro-7-methoxyisatin, m. p.  $240^\circ$ , from chloro-*ω*-oximinoacetanisidide; isatin-7-carboxylic acid, m. p.  $235^\circ$ , from *ω*-oximinoacetylthranilic acid; 5-chloroisatin from *p*-chloro-*ω*-oximinoacetanilide; 4:7-dichloroisatin, orange-yellow crystals, from 2:5-dichloro-*ω*-oximinoacetanilide; *N*-ethyl-*ψ*-isatin, dark red crystals, from *ω*-oximinoaceto-

ethylanilide; *N*-benzyl- $\psi$ -isatin, orange-yellow substance, from  $\omega$ -oximinoacetobenzylanilide. H. W.

**Changes in the Physical State of Colloids. XXIII. Acid-albumin.** MONA ADOLF and ERNST SPIEGEL (*Biochem. Zeitsch.*, 1920, **104**, 175—189).—In the conversion of serum-albumin into acid-albumin by the action of boiling hydrochloric acid, the protein molecule changes in its acid-combining, but not in its alkali-combining, power. One gram of acid-albumin combines at most with 2.5 millimols. of sodium hydroxide, the equivalent weight of the acid-albumin being thus 416, which is the value found for the natural serum-albumin. The acid-combining power of acid-albumin is, however, 20% higher than that of the albumin itself. The values for the viscosity of acid-albumin solution are higher than those of the protein, but they exhibit the same changes on addition of acid or alkali, these changes being hence due to similar ionisation influences.

On addition of alkali hydroxide or acid to a solution of the natural albumin, the rotatory power reaches a maximum corresponding with the maximum of acid or alkali-combining power, this maximum persisting even when the excess acidity for a 1% solution amounts to 0.1*N*. When hydrochloric acid is added to an acid-albumin solution, the rotatory power changes and shows a distinct maximum at 0.058*N*-acidity, but diminishes at higher acidities; the maximum rotation corresponds, not with the maximum of ionisation indicated by the viscosity curve, but with an appreciably higher acidity. According to conductivity measurements, acid-albumin in neutral salts is tervalent, the velocity of migration being  $V = 41.1$ .

Addition of salts of the heavy metals precipitates acid-albumin when dissolved in sodium hydroxide solution, but not when dissolved in hydrochloric acid; this precipitation hence represents a reaction only for the negative protein ion. T. H. P.

**Changes in the Physical State of Colloids. XXIV. Precipitation of Protein by Acids and Alkalis.** RICHARD WAGNER (*Biochem. Zeitsch.*, 1920, **104**, 190—199. Compare Pauli and Handovsky, A., 1909, i, 618; Pauli and Wagner, A., 1910, ii, 830).—Results are given of investigations on (1) the concentrations of a number of different acids just sufficient to produce flocculation in serum-albumin, (2) the viscosities of serum-albumin containing various acids in the concentration 0.05*N*, and (3) the swelling of gluten in 0.05*N*-acid. From these results, the conclusions are drawn that the state of the protein salt, as regards hydration and ionisation, conditions the precipitability of this salt in excess of acid, and that there is no reason to suppose that this precipitability is not primarily to be considered as displacement of a salt from solution by excess of its acid.

According to the author's views on the mode of salt-formation between alkali and protein, relations similar to the above should

hold in this case, and this is actually found with pure serum-albumin and alkali hydroxide in concentrations exceeding 5*N*.

T. H. P.

**Some Properties of Serin.** M. PIETTRE and A. VILA (*Compt. rend.*, 1920, **171**, 371—373).—Serin, as prepared from the serum of horse blood by the method previously described (*ibid.*, 170), is soluble in water even after drying at 40° or in a vacuum over sulphuric acid. It has  $[\alpha]_D -57^\circ$  to  $-58^\circ$ , and contains much higher percentages of sulphur and calcium than the corresponding serum globulin. It exhibits the property of separating from its solution in an almost solid, granular mass at 0°, and dissolving again at the ordinary temperature.

W. G.

**Changes in the Physical Condition of Colloids. XXII. The General Chemistry of the Caseinates. II.** WOLFGANG PAULI and JOHANN MATULA (*Biochem. Zeitsch.*, 1919, **99**, 219—236. Compare Pauli, A., 1915, i, 1016).—Conductivity experiments show that there are two zones in the reaction of casein with alkali hydroxide. In one zone, in which the reaction is neutral, the valency of the caseinate ions remains constant, whilst the conductivity increases slightly. In the second zone, when more alkali is added, both the valency and the conductivity of the caseinate ions increase. It is deduced from the conductivity curves that there exists a neutral tribasic caseinate which can take up more caseinogen without changing its valency.

S. S. Z.

**Causes of the Conductivity of Casein Solutions. I.** MÁNDOKI and M. POLÁNYI (*Biochem. Zeitsch.*, 1920, **104**, 254—258).—Measurements of the electrical conductivity of neutral casein solutions show that the protein in solution is not a good conductor, so that the conductivity of these solutions must be due largely to decomposition products of the casein (compare Laqueur and Sackur, A., 1903, i, 300; Robertson, "Physical Chemistry of the Proteins").

T. H. P.

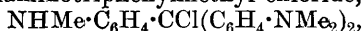
**Benzene Derivatives in Glutin and Protein-content of Gelatin.** E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1920, **109**, 32—48. Compare A., 1919, i, 502).—The author has investigated the benzene derivatives formed when the best commercial gelatin is subjected in solution at 40° to the action of a maceration of putrefying meat in presence of potassium dihydrogen phosphate, magnesium sulphate, sodium carbonate, and, in some cases, sodium potassium tartrate. The products identified comprise: (1) Traces of an indole derivative. (2) About 0.11% of aromatic hydroxy-acids, calculated on the anhydrous, ash-free material, indicating that gelatin contains the tyrosine group in appreciable proportion; succinic acid, derived from the aspartic acid of the gelatin, is also

found in small quantity. (3) At least 1·3% of phenylpropionic acid. It has also been found possible to isolate a protein from gelatin.

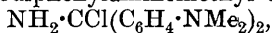
T. H. P.

**Prosthetic Group of Blood Pigment. Action of Diazomethane on certain Colouring Matters and on Anhydrous Ferric Chloride.** WILLIAM KÜSTER (*Zeitsch. physiol. Chem.*, 1920, 109, 108—116).—According to the ordinary formula for hæmin, the chlorine is assumed to be united to iron, although union with nitrogen is not excluded. In the action of diazomethane on different hæmins showing marked differences as regards esterification, removal of the halogen has never been observed. The author [with O. KUSCH] has now investigated the action of diazomethane on the hydrochlorides of various colouring matters of known constitution, and also on anhydrous ferric chloride. The results obtained indicate that true hæmins are allied rather to this anhydrous chloride, which is altered but little by diazomethane, than to the hydrochlorides of di- and tri-phenylmethane dyes, from which hydrogen chloride is very easily withdrawn, with formation of methyl chloride. With the hydrochloride of a furylmethylindolenylmethane, the reaction is less ready, and with crystal-violet reduction to the leuco-base takes place. Finally, with a rhodamine hydrochloride no esterification occurs, so that the carboxyl group cannot be free, and an oxonium grouping must be assumed (compare Noelting and Dziewoński A., 1905, i, 935).

The action of diazomethane on *Pyocyaninum coeruleum*, that is, on pentamethyltriaminotriphenylmethyl chloride,

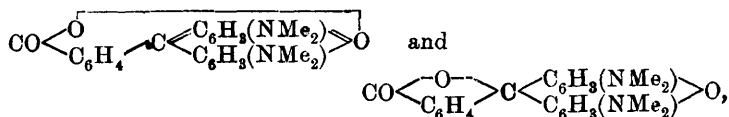


results in removal of 86·7% of the halogen. With *P. aureum*, that is, tetramethyldiaminodiphenylaminomethyl chloride,



79·2% of the chlorine is withdrawn.

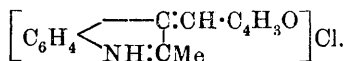
Tetramethylrhodamine hydrochloride,  $\text{C}_{24}\text{H}_{23}\text{O}_3\text{N}_2\text{Cl}$ , obtained from dimethyl-*m*-aminophenol and phthalic anhydride, forms green plates with metallic lustre, m. p. (dry) 288—290°, and dissolves in water or alcohol, giving a carmine-red solution showing orange-yellow fluorescence. The free base is obtained in green leaflets exhibiting metallic lustre, and dissolves sparingly in ether or light petroleum, and more readily in benzene, toluene, or xylene, giving colourless solutions. The constitutions of the coloured and colourless modifications of the base are



respectively. In benzene solution, the anhydrous base is unaltered by diazomethane, which, however, withdraws 97·4% of the chlorine from the hydrochloride, but does not esterify the base. The methyl ester of tetramethylrhodamine,  $\text{C}_{25}\text{H}_{26}\text{O}_4\text{N}_2$ , obtained by passing

hydrogen chloride into a solution of the hydrochloride in methyl alcohol, forms violet-red needles, m. p.  $190^{\circ}$ , is insoluble in 5% sodium carbonate solution at the ordinary temperature, but dissolves, with hydrolysis, in cold 1% sodium hydroxide solution, giving a red solution; it is soluble also in hydrochloric acid with a red coloration.

*Furyl- $\alpha$ -methylindolenylmethane hydrochloride,*



prepared from furfuraldehyde and 2-methylindole, forms spherical aggregates, m. p.  $300^{\circ}$  (decomp.), the base being obtained as a brown precipitate on addition of sodium hydroxide solution. When suspended in acetone and treated with diazomethane, the hydrochloride loses nearly all its chlorine.

From an ethereal solution of ferric chloride, diazomethane withdraws 6.71% of the chlorine.

T. H. P.

**Calorimetric Investigations on Melanins.** FRANZ VON HOEFT (*Biochem. Zeitsch.*, 1920, **104**, 1—8).—With the object of obtaining information indicative of the mechanism of formation of melanins, the author has determined the heats of combustion of various melanin preparations and of certain allied acids. The view that the formation of melanins in the integuments has its origin in tyrosine, or in the dihydroxyphenylalanine resulting from the oxidation of tyrosine, is not controverted by the author's results, the heat of combustion of tyrosine being of the same order of magnitude as that of the hippomelanin and that of one of the two liver melanins examined. On the other hand, the melanoidic acids formed during the hydrolysis of proteins by concentrated mineral acids are almost undoubtedly derived from tryptophan.

T. H. P.

**Hippomelanin. III.** OTTO RIESSER and PETER RONA (*Zeitsch. physiol. Chem.*, 1920, **109**, 16—31).—The authors have repeated and extended their earlier work (A., 1908, i, 1028; 1909, i, 749) on the decomposition of hippomelanin by the action of 3% hydrogen peroxide solution. The results obtained show that the criticisms of Adler-Herzmark (A., 1913, i, 500) are not justified, and that the experiments made by this author were inadequate.

Great difficulty is experienced in ridding the melanin of admixtures, but, after thorough purification, the preparations obtained always gave guanidine and ether-soluble acids in small yields when subjected to oxidising decomposition by means of hydrogen peroxide. That the proportion of guanidine separated represents only a minimal value is shown by the observation that guanidine carbonate is largely destroyed by hydrogen peroxide at steam-bath temperature. When the action of the hydrogen peroxide is sufficiently protracted, a large proportion of the carbon of the melanin undergoes oxidation to carbon dioxide. Gradual

oxidation of melanin by means of hydrogen peroxide in ammoniacal solution promises to yield more characteristic decomposition products.  
T. H. P.

**Relation of the Free Amino-groups to the Lysine Content in Proteins.** K. FÉLIX (*Zeitsch. physiol. Chem.*, 1920, 110, 217—229).—The author has estimated the nitrogen titratable with formalin in hydrolysed and unhydrolysed arachin (from *Arachis hypogaea*), glycinin (from *Soja hispida*), and gelatin, and draws the conclusion that the fraction of the hydrolysed protein which is precipitated by phosphotungstic acid after the removal of the other diamino-acids contains another nitrogenous substance besides lysine. The author further considers that Van Slyke's assertion (A., 1914, i, 212) that the free amino-groups of unhydrolysed proteins contain exactly one-half of the nitrogen of the lysine in the protein molecule is not justified. He suggests that the grouping of the amino-acids in the molecule may vary with the individual protein.  
S. S. Z.

**Chemical Constitution of Adenine Nucleotide and of Yeast-nucleic Acid.** W. JONES (*Amer. J. Physiol.*, 1920, 52, 193—202).—When adenine nucleotide is hydrolysed by 5% sulphuric acid at 100°, the purine group is split off much more rapidly than the phosphoric acid; further, adenine nucleotide is a dibasic acid, indicating that only one hydrogen of the phosphoric acid has been replaced. These facts necessitate the union of phosphoric acid to carbohydrate, and that, in turn, to adenine. The structure of adenine nucleotide is thus similar to that of guanine nucleotide (A., 1917, i, 597). When yeast-nucleic acid is hydrolysed with mineral acid, the rate at which phosphoric acid is set free corresponds practically with the composite rate calculated for a mixture of the four nucleotides. If yeast-nucleic acid is a chemical combination of the four nucleotides, then in this union the phosphoric acid group of the nucleotides is not disturbed and the nucleotide linkings cannot be through phosphoric acid groups. Adenine and guanine are split off from their respective nucleotides and from yeast-nucleic acid by acid hydrolysis with equal rapidity. This shows that in yeast-nucleic acid the linkings cannot be through the purine groups, and probably not through the pyrimidine groups. By this process of elimination, the nucleotide linkings in yeast-nucleic acid must be through the only remaining group, namely, the carbohydrate.  
CHEMICAL ABSTRACTS.

**Action of Boiled Pancreas Extract on Yeast-nucleic Acid.** W. JONES (*Amer. J. Physiol.*, 1920, 52, 203—207).—When an aqueous extract of pig pancreas is boiled and filtered, all its active agents but the one that decomposes yeast-nucleic acid into nucleotides, are destroyed. The extract will not act on thymus-nucleic acid. When yeast-nucleic acid is converted into nucleotides by this active agent, there is not the slightest change in acidity. This is regarded as the crucial test which proves that the nucleotide

linkings in yeast-nucleic acid are not through phosphoric acid groups. A structural formula for yeast-nucleic acid is suggested having the nucleotide linkings through the carbohydrate groups (compare preceding abstract).

CHEMICAL ABSTRACTS.

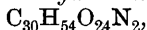
**Preparation of Adenine Nucleotide by Hydrolysis of Yeast-nucleic Acid with Ammonia.** W. JONES and A. F. ABT (*Amer. J. Physiol.*, 1920, **50**, 574—578).—Adenine-uracil-dinucleotide as prepared by Jones and Germann (A., 1916, i, 515) appears to be a mixture of adenine nucleotide and uracil nucleotide. Using the method of Jones and Kennedy (A., 1919, i, 360), the authors separated from the mixture adenine nucleotide, which had the composition required by the formula  $C_{10}H_{14}O_7N_5P.H_2O$ . The mother liquor from the adenine nucleotide yielded the brucine salt of uracil nucleotide.

CHEMICAL ABSTRACTS.

**Carbohydrate Derivatives of the Mucoids and Mucins.** O. SCHMIEDEBERG (*Arch. expt. Path. Pharm.*, 1920, **87**, 31—47).—The hyaloidin content of the mucoids and the mucins is calculated from the analytical results obtained by other investigators for some of these compounds. In the case of ovomucoid, the author also calculates the hyaloidin from the reduction figures obtained by hydrolysing the compound with hydrochloric acid. The communication contains a theoretical discussion of a series of compounds containing hyaloidin.

S. S. Z.

**Nitrogenous Carbohydrate Compounds of Protein.** O. SCHMIEDEBERG (*Arch. expt. Path. Pharm.*, 1920, **87**, 1—30).—Nitrogenous products, termed by the author hyaloidin, were obtained as cleavage products from egg-white, ovarian fluid, mucin from pig's stomach, and fibrin. Egg-white was treated with 2—3% potassium hydroxide solution at the ordinary temperature until it dissolved, and then boiled for four to five hours with 10% alkali. After precipitating the protein with acetic acid, the concentrated filtrate was treated by the copper-potassium hydroxide method, and further traces of protein were precipitated with alcohol. The hyaloidin was then obtained from this fraction either by precipitation with lead acetate or by treatment with hydrogen peroxide, and contained copper and chlorine. *Hyaloidin* prepared from ovarian fluid has the composition  $C_{26}H_{46}O_{20}N_{2.4}H_2O$ . This hyaloidin and that obtained from *Echinococcus* have the same reducing capacity after boiling with hydrochloric acid. Hyaloidin obtained from egg-white had a similar composition and the same reducing power. Hyaloidin derived from mucin of pig's stomach also shows a reducing capacity of the same order. The author concludes that hyaloidins from the above sources are identical, and suggests that the molecule contains two glucosamine, two hexose, and one acetyl group. *Fibrin-hyaloidin* obtained from fibrin,



is different from those already discussed, and, in the author's

opinion, contains two glucosamine and three hexose groups, one of which is lævulose. The structure of the compound is discussed.

S. S. Z.

**Theory of the Action of Diastase.** GERTRUD WOKER (*Biochem. Zeitsch.*, 1919, **99**, 307—316).—A reply to Wohlgenuth's criticism (*A.*, 1919, i, 361) of the author's theory of the action of diastase.

S. S. Z.

**Formation of the Gum, Levan, by Mould Spores. I. Identification and Estimation. II. Mode of Formation and Influence of Reaction.** NICHOLAS KOPELOFF, LILLIAN KOPELOFF, and C. J. WELCOME (*J. Biol. Chem.*, 1920, **43**, 171—187).—Mould spores (*Aspergillus sydowi*, Bainier) contain an enzyme capable of forming gum in sucrose solutions of all concentrations up to the saturation point. The gum is levan, m. p. about 200°; it yields lævulose on hydrolysis, and in the pure condition has  $[\alpha] -40.9^\circ$ . The invertase method may be applied to the estimation of sucrose in the presence of gum. The gum itself may be estimated polariscopically by using a combination of the Clerget and invertase methods.

Levan is formed by levanase from mould spores most readily from "nascent" dextrose and lævulose, but it appears that the latter is utilised to a greater extent than the dextrose. Only a slight formation of gum was obtained with reducing sugars in the absence of sucrose. The activity of levanase is influenced by the reaction of the medium. The optimum reaction occurs at about  $p_H$  7.0.

J. C. D.

**Preparation of Highly Active Saccharases. III. The Purification of F-preparations by Dialysis.** H. VON EULER and OLOF SVANBERG (*Zeitsch. physiol. Chem.*, 1920, **110**, 175—190).—Several of the authors' saccharase F-preparations were submitted to fractional dialysis through a collodion membrane. It was found that the carbohydrate content of the enzyme increased as the dialysis proceeded until a point was reached at which it became stationary. The authors are therefore of opinion that saccharase must consist chiefly of carbohydrates. On the other hand, the nitrogen content of the dialysed saccharase diminished and reached a limit rather higher than that obtained previously (*Zeitsch. physiol. Chem.*, 1919, **109**, 65). These experiments show that saccharase does not require a co-enzyme for its function. S. S. Z.

**Toxic Actions in Enzymic Processes. I. Inactivation of Saccharase by Heavy Metals.** H. VON EULER and OLOF SVANBERG (*Fermentforsch.*, 1920, **3**, 330—393; from *Chem. Zentr.*, 1920, iii, 200—201).—The experiments were performed by observing the inversion of sucrose by the saccharase solution used previously (*Zeitsch. physiol. Chem.*, 1919, **107**, 273). It is found that the toxic power of the silver ion towards saccharase is considerably



greater than that of the mercuric ion. The enzyme is thereby inactivated, but not destroyed, since its power is completely restored by removal of the heavy metal or by converting it into an insoluble form (by hydrogen sulphide). The graph showing the relationship between toxicity and concentration in the case of mercuric chloride resembles the dissociation curve, whereas complete proportionality is found in the case of silver nitrate. The substrate (sucrose) exercises a considerable protective action towards metallic poisoning, which must be taken into account in calculating the necessary amount of poison per enzyme unit. With small amounts of mercuric chloride, the coefficient of inversion falls rapidly with the time. The degree of poisoning also depends on the length of time during which the mercuric chloride and saccharase are in contact previous to inversion; "self-regeneration" of the enzyme occurs gradually, the process appearing to be analogous to the "Danysz" effect in immunochemistry. The concentration of free silver ions becomes greatly diminished after addition of the enzyme solution to a dilute solution of silver nitrate, but metallic or colloidal silver is not formed, so that it would appear that union occurs with some components of the enzyme solution; it is found by electrometric measurement that each c.c. of enzyme solution (containing 56 mg. of dry substance) requires from 28 to 55 mg. of silver. The toxic action of auric chloride towards saccharase is of the same order as that of mercuric chloride, whilst copper sulphate is much less poisonous, and cadmium sulphate, thallium sulphate, and uranium nitrate are scarcely toxic.

The previous data concerning the inhibition of enzyme actions by heavy metals are collected.

H. W.

**Artificial Zymogens.** MARTIN JACOBY (*Biochem. Zeitsch.*, 1920, 104, 316—322).—The name artificial zymogen is given to enzymes inactivated by nickel or by mercuric chloride, this inactivation being assumed to be due to the formation of complex compounds of the enzyme with the inactivating substance.

Inactivation of urease is effected by means of minimal proportions of nickelous oxide, whereas a somewhat large quantity of the undissolved metal is required for the same purpose; it is now found that only the slight traces of metal passing into solution are active in this respect. In order to decide whether the nickel combines with the enzyme molecules or whether the metal in the free state in solution prevents the enzymic action, inactivated urease solution was subjected to dialysis, its action on carbamide being then examined both before and after activation by means of potassium cyanide. It is found that the zymogen is not activated by dialysis alone, but remains in the dialysed solution. The conclusion is drawn that the nickel forms an actual compound with the enzyme. Experiments made in presence of glycine indicate that the nickel enters the amino-acid compound, thus leaving the zymogen and escaping dialysis; in this way, the enzyme is rendered active.

T. H. P.

**Preparation of *o*-Guätholmonomethyltrioxyarsenomenthol.**

ALFRED MAUERSBERGER (D.R.-P. 320797; from *Chem. Zentr.*, 1920, iv, 293).—(i) Mentholguätholsulphuric ester is condensed with disodium monomethyl arsenate. (ii) Sodium benzenedisulphonate is treated with sodium ethoxide, and subsequently with sodium arsenite; the intermediate product so obtained is treated with methyl menthylsulphate. Mentholguätholsulphuric ester is a brown, oily liquid. The final product is a viscous mass, which solidifies at about 22° and has b. p. 154° (decomp.); it is expected to find application in pharmacy.

H. W.

**Synthesis of Boranilides. I. Boranilide and its Derivatives.** TARINI CHARAN CHAUDHURI (T., 1920, 117, 1081—1086).

**Elements of the Oxygen Group and Organo-magnesium Compounds.**

M. GIUA and F. CHERCHI (*Gazzetta*, 1920, 50, i, 362—377).—The action of tellurium on magnesium phenyl bromide is similar to that of sulphur or selenium, and results in the formation of phenyl telluromercaptan, diphenyl ditelluride, phenyl telluride, and, in small proportion, hydrogen telluride: (1)  $\text{MgPhBr} + \text{Te} = \text{Ph} \cdot \text{Te} \cdot \text{MgBr}$ , and the latter  $+ \text{HCl} = \text{MgClBr} + \text{TePhH}$ ; (2)  $2\text{MgPhBr} + 2\text{Te} = \text{TePh}_2 + \text{Te}(\text{MgBr})_2$ , and the latter  $+ 2\text{HCl} = \text{TeH}_2 + 2\text{MgClBr}$ . The amount of hydrogen telluride indicated by equation (2) is, however, greater than that actually formed when the complex is treated with dilute acid. The formation of phenyl telluride appears to be due to decomposition of the phenyl telluromercaptan, as this readily undergoes oxidation to diphenyl ditelluride, which decomposes into tellurium and phenyl telluride.

The action of sulphur, selenium, or tellurium on magnesium pyrrol iodide yields black, infusible compounds which, from their properties, are pyrrole-blacks containing, respectively, sulphur, selenium, and tellurium (compare Angeli and Pieroni, A., 1919, i, 134). These results indicate the complete chemical analogy existing between tellurium and the other elements of Group VI of the periodic system. The possible existence of isotopes in the case of tellurium is discussed.

Phenyl telluromercaptan,  $\text{PhTeH}$ , is unstable, but with mercuric chloride forms the compound,  $\text{TePh} \cdot \text{HgCl}$  (compare Lederer, A., 1915, i, 1056), m. p. 85—90° (decomp.); it yields also a grey *aurichloride*, m. p. 154—156°, and a yellow, amorphous *platinichloride*, m. p. 75—80°.

The products obtained by the action of tellurium on magnesium phenyl bromide were fractionated at a pressure of 85 mm. When treated with concentrated sulphuric and nitric acids, the fraction having b. p. 155—200° yields a pale yellow, amorphous substance [ $?( \text{NO}_2 \cdot \text{C}_6\text{H}_4 )_2 \text{TeO}$ ], which contains 6.44% N and does not melt at 250°.

The residue failing to distil at 200° gives, when treated with concentrated nitric acid, (1) phenyltelluric acid nitrate,  $\text{C}_6\text{H}_5\text{O}_4\text{NTe}$ , m. p. 210—212° (Lederer, *loc. cit.*, gave m. p.

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232—233°); the latter is decomposed by sodium hydroxide, giving the compound,  $O(\text{TePh}_2\cdot\text{NO}_3)_2$ , m. p. 223—224° (compare Lederer, *loc. cit.*). (2) A compound which separates in minute, shining, white crystals, m. p. 66—68°, and at a higher temperature becomes solid, and then has m. p. 201—203° (decomp.); this compound loses 2·89% at 80—90°, the formula  $O\cdot\text{TePh}\cdot\text{NO}_3\cdot 2\text{EtOH}$ , corresponding with 2·46% of alcohol, and  $\text{Te}_2\text{O}_7\cdot\text{N}_2\text{Ph}_4\cdot 6\text{EtOH}$  with 2·82%.

The same fraction (above 200°) reacts energetically with bromine in ethereal solution, giving the compound,  $\text{Te}_2\text{Br}_4\text{Ph}_2$ , which forms shining, yellow crystals, m. p. 200°, becoming opaque in the air, and loses part of its bromine when treated with alkali carbonate or hydroxide.

Analysis of the black compound resulting from the action of sulphur on magnesium pyrryl iodide gave: N 13·06—13·37, S 21·67, and ash 0·205%.  
T. H. P.

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### Physiological Chemistry.

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**Relative Value of Fat and Carbohydrate as Sources of Muscular Energy. With Appendices on the Correlation between Standard Metabolism and the Respiratory Quotient during Rest and Work.** AUGUST KROGH and JOHANNES LINDHARD [with GÖRAN LILJESTRAND and KNUD GAD ANDERSEN] (*Biochem. J.*, 1920, **14**, 290—361).—An elaborate and valuable study of this important question. A method of determining the respiratory exchange of human subjects is described which admits of a high degree of accuracy. All the results agree in showing that work is more economically performed on carbohydrate than on fat. A hypothesis regarding the physiological utilisation of fat and carbohydrate during work is advanced. J. C. D.

**Habituation to Bromine Vapour and Action of the Latter on the Blood.** S. MARINO (*Arch. farm. sper. sci. aff.*, 1920, **29**, 48—64).—Respiration of bromine vapour causes diminution of the number of red corpuscles and of the content of hæmoglobin in the blood. The extent of this diminution increases with the quantity of the vapour administered, but not with repetition of the treatment. Habituation of the animal organism to bromine vapour is attainable by gradual increase of the dose, but even continued small doses produce hæmolysis. The vapour conditions marked increase in the leucocytes, sometimes to about four times their normal number. T. H. P.

**Injurious Action of Carbon Dioxide on Red Blood Corpuscles.** W. PATZSCHKE (*Zeitsch. physiol. Chem.*, 1920, **109**, 1—11).—Experiments in vitro show that carbon dioxide increases

by fifty or one hundred times the action of inorganic blood poisons which form methæmoglobin, the incidence of the reaction being accelerated markedly by rise of temperature. In presence of aniline or nitrobenzene, the formation of methæmoglobin in human blood occurs only after introduction of carbon dioxide. It is therefore probable that the development of the action of certain poisons in the veins is brought about by the carbon dioxide present. Intensification of the formation of methæmoglobin by carbon dioxide is produced, not only in suspensions, but also in solutions of blood corpuscles and in hæmoglobin solutions, so that it may be assumed that the carbon dioxide induces changes in the hæmoglobin favourable to the formation of methæmoglobin. Blood corpuscles charged with carbon dioxide are labile cells readily accessible to injury, whereas oxygen protects the corpuscles.

T. H. P.

**Antigens and Serological Specificity. XIV. Specific Serum Reactions with Simple Compounds of Known Constitution (Organic Acids).** KARL LANDSTEINER (*Biochem. Zeitsch.*, 1920, 104, 280—299. Compare this vol., i, 260).—The experiments now described show that with diazotised aniline-*m*-sulphonic acid, *p*-arsanilic acid, *o*-toluidine-5-sulphonic acid coupled with tyrosine, *m*-hydroxybenzoic acid, and salicylic acid the precipitin reactions of the corresponding azo-proteins are completely or almost completely destroyed; the action is a specific one, the specificity resembling that of the precipitin reactions of the azo-proteins themselves. Not only are the precipitations prevented by these azo-compounds, but with the help of the latter the precipitates, when formed, may, after centrifugation and washing, be dissolved. These inhibiting substances contain a group identical with the specific group of the corresponding azo-protein with which the immune serum employed reacts. The assumption may therefore be made that the inhibiting body combines with the anti-substance of the immune serum, and so prevents this from acting on and precipitating the azo-protein present in the solution. Such specific serum reactions with synthetic compounds of known constitution represent a new discovery.

Experiments have been made with simpler compounds in the same way as with the azo-colouring matters. As regards the azo-components corresponding with the immune sera, sodium *m*-aminobenzenesulphonate and *p*-aminophenylarsinate in neutral solution exhibit selective inhibiting action. In equimolecular proportions, the azo-colouring matters act considerably more strongly than the simple amino-acids, although these act at moderately low concentrations. The connexion between inhibiting effect and chemical constitution has further been investigated with a large number of other compounds, such as amino-acids and carboxylic, sulphonic, and arsinic acids free from amino-groups.

Of the various monobasic, polybasic, saturated, unsaturated, and substituted aliphatic carboxylic acids, most produce no, and none marked, inhibition of the precipitin reaction with the immune sera. With the aromatic and cyclic carboxylic acids, the action depends

on the constitution. The results obtained with benzene derivatives depend less on the character of the substituents than on their position, although the carboxyl group has a somewhat greater influence than other substituent groups. The results obtained are given in detail and discussed.

T. H. P.

#### **Formation of Protein from Carbamide by Ruminants.**

E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1920, **109**, 276—279).—As regards the source of the sulphur of the protein formed in sheep fed with straw previously treated with sodium hydroxide (this vol., i, 699), it appears that the sheep were supplied with various inorganic salts, including potassium sulphate and sulphide. Estimation of the sulphur in the ash of straw treated with sodium hydroxide according to Beckmann's method shows that it is only just sufficient, if completely utilisable, to furnish the sulphur of the flesh formed by the sheep during the experiment; if the organically-bound sulphur of the straw is included, more than sufficient sulphur is supplied. The source of the tryptophan still remains an open question.

T. H. P.

**Taurine from Herring Flesh and its Crystallographic Investigation.** E. BERNER (*Zeitsch. physiol. Chem.*, 1920, **110**, 172—174).—The author has separated about 0.003% of taurine from the flesh of the herring (*Clupea harengus*), and has obtained it in exceptionally well-developed crystals belonging to the prismatic class of the monoclinic system:  $a:b:c = 0.6817:1:0.9073$ ,  $\beta = 93^\circ 47'$ .

T. H. P.

**Formation of Oxalic Acid in the Animal Body.** LUDWIG PINCUSOHN (*Biochem. Zeitsch.*, 1919, **99**, 276—297).—Nucleic acid, xanthine, guanine, uric acid, and allantoin when introduced into the system of dogs and rabbits, either per os or by intravenous injection, produce an increase in the content of oxalic acid and a decrease in the allantoin content of the urine. The uric acid remains constant. Similar observations were made in a more pronounced way when the substances were previously "sensitised" and exposed to light.

S. S. Z.

**Amino-acid Synthesis in the Animal Organism. Can Norleucine Replace Lysine for the Nutritive Requirements of the White Rat?** HOWARD B. LEWIS and LUCIE E. ROOT (*J. Biol. Chem.*, 1920, **43**, 79—87).—Eighteen per cent. of gliadin as the sole source of protein in the diet of a young rat will not permit growth until the inadequacy of lysine is made good. Neither *dl*-norleucine nor *d*-norleucine is able to supply the deficiency of a gliadin diet as does a supplement of lysine.

J. C. D.

**Relation of Urochrome to the Protein of the Diet.** K. F. PELKAN (*J. Biol. Chem.*, 1920, **43**, 237—242).—The excretion of

urochrome appears to be dependent on the amount of protein in the diet.

A substance, protochrome, which gives similar reactions to urochrome, can be produced from certain proteins. All evidence points to the fact that urochrome, lactochrome, and protochrome are identical, and, at least to a large extent, are derived from the food proteins.

J. C. D.

**Presence of Iodine in Large Quantities of Sheep Pituitary Glands.** EMILY C. SEAMAN (*J. Biol. Chem.*, 1920, **43**, 1—2).—No iodine was detected in quantities of sheep pituitary gland as large as 100 grams (compare Denis, A., 1911, ii, 746).

J. C. D.

**Decomposition Products of Atractylin in the Animal Organism.** A. PITINI (*Arch. Farm. sper. Sci. aff.*, 1920, **29**, 88—96).—In an alkaline medium, atractylin, which has the probable formula  $C_{30}H_{52}O_{18}S_2K_2$ , decomposes, yielding sulphuric and valeric acids, a carbohydrate, and a complex product (A), which is obtained as a white powder, and gives the following reactions: in concentrated sulphuric acid containing traces of formaldehyde it dissolves to a red solution, which is turned deep blue by addition of a small quantity of water; with concentrated sulphuric acid and a few drops of aqueous vanillin solution, it yields an intense carmine-red coloration. By means of these reactions, the gastro-intestinal contents and various organs of a dog poisoned with atractylin were shown to contain this product A.

T. H. P.

**Relation of Hyaloidin to the Formation of Chondroitin-sulphuric Acid, Collagen, and Amyloid in the Organism.** O. SCHMIEDEBERG (*Arch. expt. Path. Pharm.*, 1920, **87**, 47—74).—A theoretical paper containing a critical discussion of the above subject.

S. S. Z.

**The Existence in the Bile of an Inhibitor for Hepatic Esterase, and its Nature.** GEORGE MACFEAT WISHART (*Biochem. J.*, 1920, **14**, 406—417).—An inhibitory substance for the esterase of liver was found to be present in the bile of all the animals examined. It is probably the cholic acid portion of the bile acid molecules which is responsible for the effect.

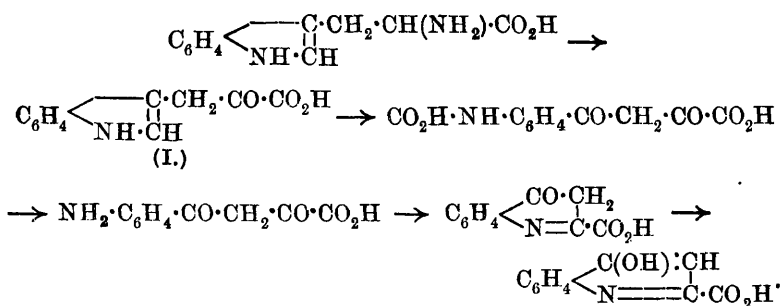
J. C. D.

**Bioluminescence. I. The Luciferin and Luciferase of *Cypridina hilgendorffii*. II. The Production of Light by *Cypridina hilgendorffii* is not an Oxidation.** S. KANDA (*Amer. J. Physiol.*, 1920, **50**, 244—260, 561—573).—I. Two substances, corresponding with luciferin and luciferase found by Dubois in *Pholas dactylus*, are concerned in the production of light by *Cypridina hilgendorffii*. The first is thermostable; the second is destroyed by heat. Both are produced only in the maxillary gland cells of the animal. The author is of opinion that Harvey's theory and nomenclature (A., 1917, i, 365) are not tenable. II. The

intensity of light produced by *Cypridina* in recently boiled water saturated with various gases was strongest in hydrogen and weakest in oxygen. Saturation with carbon monoxide, carbon dioxide, or nitrogen gave lights of intermediate intensities. It is concluded that the light cannot be produced by oxidation.

## CHEMICAL ABSTRACTS.

**Formation of Kynurenic Acid from Tryptophan in the Animal Body.** A. ELLINGER and Z. MATSUOKA (*Zeitsch. physiol. Chem.*, 1920, **109**, 259—271. Compare A., 1914, i, 865).—The authors have synthesised indolepyruvic acid, and find that, when this acid is administered subcutaneously as sodium salt to a dog, it is possible to isolate from the urine kynurenic acid in amount rather less than one-half of that obtained when tryptophan is injected. The conclusion is drawn that the conversion of tryptophan into kynurenic acid is best represented by the scheme (compare Dakin, "Oxidations and Reductions in the Animal Body," 1912, 73; Barger and Ewins, A., 1917, i, 476):



The condensation of indole-3-aldehyde and hippuric acid in presence of acetic anhydride and sodium acetate yields, not the azlactone (compare Ellinger and Flamand, A., 1908, i, 378), but its 1-acetyl derivative (annexed formula), which crystallises in pale yellow rhombic or oblique rhombic plates, m. p. 205—206°, and, when treated with sodium hydroxide solution, yields

Indolepyruvic acid (formula I, above), which forms yellow (+ C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>) or almost colourless crystals. Its p-nitrophenylhydrazone, C<sub>8</sub>H<sub>6</sub>N·CH<sub>2</sub>·C(CO<sub>2</sub>H):N·NH·C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub>, crystallises in rosettes of yellow plates, m. p. 153—154°.

When quinoline-2-carboxylic acid is administered as sodium salt subcutaneously to a dog, it is separated in the urine partly unchanged and partly coupled with glycine, but does not undergo oxidation to kynurenic acid.

T. H. P.

**Behaviour of Aspirin in the Animal Organism.** A. PITINI (*Arch. Farm. sper. Sci. aff.*, 1920, **29**, 113—118).—Investigation



of the urine of dogs to which aspirin had been administered indicates the presence of unchanged aspirin, so that part of the aspirin is absorbed in the animal organism before undergoing hydrolysis.  
T. H. P.

**Appearance of Acetaldehyde in the Body due to Cleavage of Ethyl Alcohol.** WILHELM STEPP (*Arch. expt. Path. Pharm.*, 1920, **87**, 148—153).—The presence of acetaldehyde was established in the blood and urine of a human subject who had previously consumed ethyl alcohol. In the case of a dog which had received ethyl alcohol, acetaldehyde was found in the urine, but not in the blood.  
S. S. Z.

**Chemistry of the Proteins. The Species Specificity of the Structure of Protein.** E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1919, **99**, 204—219).—A theoretical paper in which the structure of protein molecules in relation to immunity and heredity phenomena, and the mechanism of protein synthesis and degradation, are discussed.  
S. S. Z.

**Nature of Anaphylaxis.** EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1920, **109**, 289—297. Compare A., 1912, ii, 1194).—The authors have treated guinea-pigs by subcutaneous or intraperitoneal injection with glycine and its polypeptides up to heptaglycylglycine, but no phenomena were obtained resembling anaphylactic shock, with the exception of slight variations in the temperature. From the heptapeptide onwards, the injection causes a characteristic skin affection.

Methods are described for preparing glycine ethyl ester hydrochloride in large amounts from chloroacetic acid, and pentaglycylglycine from tetraglycylglycine and chloroacetyl chloride.

T. H. P.

**Chemical and Morphological Studies on Cholesterol and its Esters in Normal and Pathological Organs.** JOHAN FEX (*Biochem. Zeitsch.*, 1920, **104**, 82—174).—The author's investigations show that Windaus's digitonin method (A., 1910, ii, 462), as modified by Thaysen (A., 1914, ii, 498), is the only method yet described giving trustworthy results for the estimation of cholesterol in its pure solutions. Preliminary drying in a current of air of the organs from which the cholesterol and its esters are to be extracted is not to be recommended, but treatment of the organs with 2% sodium hydroxide solution and extraction of the alkaline solution with ether result in quantitative extraction and in an extract of such purity that the cholesterol and its esters may be estimated exactly by the above method.

The proportions of free and combined cholesterol in the liver show very slight variations in all the cases examined, including two of cirrhosis of the liver. In the kidneys, of both normal and diseased individuals, the free cholesterol varies but little in amount, and the same holds for the combined cholesterol, even in the cases

of diabetes, pernicious anæmia, cirrhosis of the liver, and sepsis examined; with diseases of the kidneys, however, the normal small proportion of cholesterol present as ether is considerably exceeded. Inconsiderable variations occur in the proportion of free cholesterol in the suprarenal glands, but the combined cholesterol exhibits wide differences in different cases, the highest amounts being found in two instances of kidney disease and in one normal instance. In no case examined was cholesterol detectable morphologically in the liver, but with kidney disease of long standing the ester of cholesterol may be discovered morphologically in the kidneys in amount corresponding well with that found chemically.

T. H. P.

**The Colloid Chemical Importance of Physiological Ionic Antagonism and of Equilibrated Salt Solutions.** S. M. NEUSCHLOSZ (*Pflüger's Archiv*, 1920, 181, 17—39; from *Chem. Zentr.*, 1920, iii, 312).—It has not been well established that the physiological action of ions depends solely on their relationship to the proteins, and that these relationships are purely chemical in character. In many physiological phenomena, in the cell, lipoids play a predominating rôle. Solutions of lecithin (2%) have been treated with equal quantities of salt solutions and their surface tensions determined stalagmometrically. The chlorides of the cations Na, K, Ca, Mg, and Al noticeably increase the surface tension of lecithin solutions. With mixtures of these salts, an antagonism between the cations is very obvious. The surface tension of a lecithin solution in the presence of a mixture of salts is dependent, in the first place, on the relative ratio of concentration of the cations, and is not influenced within wide limits by the absolute concentration of the solution. A far-reaching parallelism exists between physiological and colloidal chemical ionic antagonism as shown in this manner. The physico-chemical basis of ionic antagonism is found in the capacity shown by the cations of mutual replacement from their adsorption compounds (in this case from the surface of the lecithin particles), but the displacing ion does not take the place of that displaced.

H. W.

**Water-soluble Vitamines. I. Are the Antineuritic and the Growth-promoting Water-soluble-B Vitamines the Same?** A. D. EMMETT and G. O. LUKOS (*J. Biol. Chem.*, 1920, 43, 265—286).—Experiments designed to ascertain whether these two substances are identical lead the authors to suggest, tentatively, at least, that they are not the same. The antineuritic factor appears to be more readily decomposed by heat. The lack of strictly quantitative methods renders the conclusion indefinite.

J. C. D.

**Toxic Action of Cyanogen Chloride.** C. I. REED (*J. Pharm. Expt. Ther.*, 1920, 15, 301—304).—This action is primarily due

to the formation of hydrocyanic acid, but in delayed poisoning the chlorine may also have an effect. Protection may be given by sodium thiosulphate.

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J. C. D.

## Chemistry of Vegetable Physiology and Agriculture.

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**Control of the Purity of Preparations of Carbohydrate by Bacterial Fermentation Tests.** H. O. SCHMIT-JENSEN (*Compt. rend. Soc. Biol.*, 1920, **83**, 699—701; from *Chem. Zentr.*, 1920, iv, 217).—Different types of bacteria can be investigated by their action towards different carbohydrates (*Compt. rend. Soc. Biol.*, 1920, **83**, 502); conversely, the purity of carbohydrates and polyhydric alcohols can be tested by fermentative action if the necessary classes of bacteria are available. H. W.

**Proteins of Putrefactive Bacteria.** E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1920, **109**, 49—56).—Putrefactive bacteria are found to contain two protein compounds, one having the characters of the albumoses and the other those of a globulin-like protein. Neither contains the tryptophan group, whilst the atomic complex giving the xanthoprotein reaction is almost entirely lacking with the albumose and present in extremely small proportion in the protein. When heated in a narrow test-tube, both emit vapour capable of blackening lead acetate paper (Siegfried's reaction), whereas this behaviour is not shown by the proteins and is doubtful with the albumoses.

Since Siegfried's reaction was unknown to Nencki, it is possible that the latter's anthraxprotein (A., 1885, 178) is not quite free from sulphur. Further work is necessary to ascertain if unicellular organisms are able to produce proteins not lacking in cyclic and heterocyclic groups, but possibly this power is restricted to the true plants, among which bacteria and yeasts cannot be placed. Between plants and animals lies a third group of organisms, which are able to utilise inorganic nitrogen to build up their body-substance, but are unable, apparently owing to absence of chlorophyll, to convert inorganic into organic carbon.

Voeltz (*Berlin Klin. Woch.*, 1919, No. 29) fed sheep for seventeen to twenty-five days solely on straw (treated with sodium hydroxide and free from digestible nitrogen), sugar, starch, and carbamide, growth and accumulation of protein taking place. The sources of the sulphur and the tryptophan group of the protein formed are obscure. T. H. P.

**The Enzymes of B. Coli communis which are Concerned in the Decomposition of Dextrose and Mannitol. IV. The Fermentation of Dextrose in the Presence of Formic Acid.** EGERTON CHARLES GREY (*Proc. Roy. Soc.*, 1920, [B], **91**, 294—305).—The products obtained in the decomposition of dextrose by

*Bacillus coli communis* are divided into three groups: (1) lactic acid; (2) acetic acid, alcohol, and succinic acid; (3) formic acid, carbon dioxide, and hydrogen, there being a closer relationship between the products of groups (2) and (3) than exists between either group and group (1). The proportions in which the products of group (2) appear depend on the intimacy with which the reactions of this group co-operate with the reactions of group (3), and this further explains the fact that in many normal fermentations there is a tendency for groups (2) and (3) to appear as constituting one group.

It is now demonstrated that hydrogen, nascent during the fermentation, does take part in the production of alcohol, the hydrogen arising either from the decomposition of the dextrose itself or from the simultaneous fermentation of added calcium formate. It is also shown that the presence of calcium formate does not depress the formation of formic acid, and the consequent yield of its gaseous products, carbon dioxide and hydrogen, in the fermentation of dextrose by *B. coli communis*. W. G.

**Action of *Bacillus fluorescens liquefaciens* (Flügge) on Asparagine in a Definite Chemical Medium. II. Products from, and Mode of Attack on, Asparagine.** A. BLANCHETIÈRE (*Ann. Inst. Pasteur*, 1920, **34**, 392—411).—The chief products formed are acetic, malic, succinic, fumaric, and carbonic acids. The mechanism of their formation is discussed. J. C. D.

**Influence of the Nature of the Carbonaceous Food on the Utilisation of Nitrogen by *Bacillus subtilis*.** E. AUBEL (*Compt. rend.*, 1920, **171**, 478—480).—Glycerol gives a better yield of culture and a better utilisation of nitrogen than lævulose, and this in turn than dextrose, when added to the culture solution of *Bacillus subtilis*. The high yield of organism and increased utilisation of nitrogen with glycerol are probably due to its preliminary conversion into pyruvic acid, and it is noted that sodium pyruvate gives even better results than glycerol. W. G.

**Experiments on Osmosis and on Aspiration due to Evaporation, Suitable for Use in Plant Physiology.** PIERRE LESAGE (*Compt. rend.*, 1920, **171**, 358—360).—Simple modifications of the experiments of Dutrochet and Askenasy are described. W. G.

**Fluorescence and Condition of Chlorophyll in Living Cells.** KURT STERN (*Ber. Deut. bot. Ges.*, 1920, **38**, 28—35).—The author's spectroscopic investigations show that chlorophyll fluoresces only in true solution, colloidal chlorophyll solutions and solid chlorophyll exhibiting no appreciable fluorescence. Observation of the fluorescence of turbid media with the naked eye leads to erroneous conclusions, spectroscopic examination being necessary to ascertain the real strength of the fluorescence. In the intact cell, the chlorophyll is contained in lipoidal, true, and fluorescing

solution. The process of assimilation proceeds partly in the lipoidal and partly in the hydroid phase, and surface-active substances alter the limiting surface between the two phases and thereby retard or assist assimilation. T. H. P.

### **Behaviour of certain Organic Compounds in Plants. XII.**

G. CIAMICIAN and C. RAVENNA (*Gazzetta*, 1920, **50**, ii, 13—46).—An account of work already published (A., 1919, i, 58, 140, 241; this vol., i, 408). T. H. P.

### **Enzyme Formation with *Aspergillus niger*. H. von**

EULER and S. ASARNOJ (*Fermentforsch.*, 1920, **3**, 318—329; from *Chem. Zentr.*, 1920, iii, 201—202).—The investigation proceeded along lines similar to those adopted by Euler and Svanberg (A., 1919, i, 201, 614) in the case of saccharase in bottom yeast. As far as saccharase is concerned, it is found that the total enzyme action remains almost unchanged if the well-ground fungus material is brought into contact with sucrose solution either after being warmed to a temperature at which the saccharase is not damaged or after being dried with or without toluene. Wohlgemuth's method can only be applied with difficulty to the estimation of amylase by the direct action of the fungus material on starch solution; the sugar which is formed is best estimated by Bertrand's reduction method. For the type investigated, and under certain conditions, the inverting capacity,  $I_f = k \times g$  sugar/ $g$  dry substance, is found to be  $0.32 \times 10^{-2}$ . A fungus which had been grown on starch solution with the addition of peptone had a saccharase activity about 30% higher than that of a specimen grown under similar conditions but in the absence of peptone. Addition of peptone to the nutrient solution, which otherwise contains only inorganic nitrogen, also influences the formation of amylase. The data of other workers with regard to the improvement in the formation of amylase, due to addition of starch to the nutrient solution, could be quantitatively confirmed. H. W.

### **Water-soluble Vitamines. II. The Relation of the Antineuritic and Water-soluble Vitamines to the Yeast Growth-promoting Stimulus. A. D. EMMETT and MABEL**

STOCKHOLM (*J. Biol. Chem.*, 1920, **43**, 287—294).—Further evidence is given in support of the theory that the antineuritic and the growth-promoting vitamines are not identical. It is also possible that the substance which promotes cell-division in yeast is another factor of the vitamine type. It is therefore considered inadvisable to employ the quantitative method introduced by Williams (A., 1919, i, 463) until the differentiation of these factors has been satisfactorily accomplished. J. C. D.

**Comparative Studies on Respiration. XI. Effect of Hydrogen-ion Concentration on the Respiration of *Penicillium chrysogenum*. F. G. GUSTAFSON (*J. gen. Physiol.*, 1920, **2**, 617—626).**—Variations in the  $P_H$  value between 4 and 8

produce practically no effect on the normal rate of respiration of *Penicillium chrysogenum* (the rate at neutrality is considered normal). Increasing the  $P_H$  value to 8.80 causes respiration to fall to 60% of the normal, after which it remains stationary for the duration of the experiment. Decreasing the  $P_H$  value to 2.65 causes a gradual rise and a gradual return to the normal; at  $P_H$  1.10 to 1.95 the preliminary rise amounts to 20%, and is followed by a fall to below the normal. The decreases in respiration brought about by solutions of a  $P_H$  value of 1.95 or less are irreversible, whilst a similar decrease which occurs at  $P_H$  8.80 is reversible, the rate coming back to practically normal after the material is replaced in a neutral solution.

Determinations by means of Winkler's method showed an increase in the consumption of oxygen in acid solutions and a decrease in alkaline solutions.

H. W.

**Crystallisable Sugar and Free Acids in Plants.** H. COLIN (*Compt. rend.*, 1920, 171, 316—318).—The fact that sucrose exists in a large number of fruits in the presence of free acid at a concentration more than sufficient to cause its inversion is shown to be due to the presence of alkali salts of the organic acids in the juices, which lessen the hydrolysing action of the free acids.

W. G.

**Relation between the Calcium and the Nitrogen Content of Plants and the Function of Calcium.** F. W. PARKER and E. TRUOG (*Soil Sci.*, 1920, 10, 49—56).—From the consideration of a large number of analyses of various plants with respect to their nitrogen, phosphorus, potassium, calcium and magnesium content, it was observed that the only element the amount of which was closely related to the nitrogen content was calcium. These plants could be grouped in two classes, according to their calcium-nitrogen ratio. In one group the ratio was low, averaging 0.306, and this group consisted of plants of the grass family, which have a low lime requirement. In the other group the ratio was high, 0.553, and the group contained the legumes and other plants which have a high lime requirement and are sensitive to soil acidity. These results point to the conclusion that plants which have a high nitrogen or protein content, and therefore produce a large amount of acidity from protein metabolism, require a large amount of calcium as carbonate for the neutralisation of the plant acids.

J. H. J.

**Inulin in the Globe Artichoke.** RUTH OKEY and ANNA W. WILLIAMS (*J. Amer. Chem. Soc.*, 1920, 42, 1693—1696).—In a sample of globe artichoke which, by the ordinary methods of analysis of foodstuffs, gave 6.8% of nitrogen-free extractives, the authors found 2.5% of inulin and altogether 4.2% of total carbohydrate extracted by water and 1% hydrochloric acid.

W. G.

**Enzyme Action in *Echinodontium tinctorium*, Ellis and Everhart.** HENRY SCHMITZ (*J. gen. Physiol.*, 1920, 2, 613—616).—The present paper is the second of a series dealing with the

physiology of wood-destroying fungi (compare Schmitz and Zeller, *Ann. Missouri Bot. Garden*, 1919, 6, 193). In *Echinodontium tinctorium*, the presence of the following enzymes has been demonstrated: esterase, maltase, lactase, sucrase, raffinase, diastase, inulase, cellulase, hemicellulase, urease, rennet, and catalase.

H. W.

**Carbohydrates of Lichen islandicus.** E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1920, 110, 158—166. Compare A., 1919, i, 242).—The author confirms the statement of Errera (Diss., 1882) and others to the effect that *Lichen islandicus* contains two carbohydrates: (1) lichenin, which gelatinises when the hot solution is cooled and gives no reaction with iodine, and (2) a soluble carbohydrate which, contrary to the statement of Ulander and Tollens (A., 1906, ii, 193), gives a decided blue coloration when carefully treated with iodine solution; this coloration is, however, distinctly less intense than that obtained with starch, and it is possible that this carbohydrate, known as isolichenin, is not a single individual, and that the iodine reaction depends on the presence of a third carbohydrate in small proportion.

The physical constitution of lichenin in the moist state suggests that this compound either belongs to the pectins or contains these. Dry lichenin does not, however, respond to the method for detecting pectin given by von Fellenberg (A., 1916, ii, 351), according to whom the pectins yield methyl alcohol when treated with sodium hydroxide solution.

T. H. P.

**Kinetics of the Action of Catalase Extract from Marine Algæ, with a Note on Oxydase.** HAROLD CLARK HAMPTON and LOURENS G. M. BAAS-BECKING (*J. Gen. Physiol.*, 1920, 2, 635—649).—Preliminary investigations of the catalase, peroxydase, and oxydase of marine algæ are described, the present communication dealing only with *Ulva taeniata*, Setchell and Gardner. This contains a catalase, which adheres to the cells to a certain extent, but may, mechanically or by exosmosis, pass into the surrounding medium. This catalase is able to act on peroxide in a neutral medium, the reaction being unimolecular. In an alkaline medium, the catalase decomposes peroxide, following the formula of Schmidt-Nielsen,  $K = \sqrt{a} - \sqrt{a-x}/t\sqrt{a(a-x)}$ . The reaction time varies in a linear relation with the concentration of the peroxide. Reaction velocity and enzyme concentration vary in a linear relation. Reaction velocity and peroxide concentration vary in a continuous non-linear and non-exponential relation. Since the peroxide is in excess of the feeble catalase, these facts are in agreement with the data of Senter on blood catalase. On dilution, the enzyme is destroyed, following highly exponential lines,  $dx/dt = K(a-x)^3$ , or even  $dx/dt = K(a-x)^4$ .

*Ulva taeniata* contains oxydase; the presence of peroxydase is not proved.

H. W.



**Extractive Substances of *Melolontha vulgaris*.** DANKWART ACKERMANN (*Zeitsch. Biol.*, 1920, **71**, 193—202).—This organism is found to contain uric acid, leucine, putrescine, lysine, *p*-hydroxyphenylethylamine, choline, and either cholesterol or an allied sterol. Melolonthine (compare Schreiner, A., 1871, **24**, 1201), creatine, creatinine, betaine, and tyrosine could not be detected.

T. H. P.

**Action of Rain Water on the Deposits from Copper Spray Liquids.** G. VILLEDIEU and (MME) VILLEDIEU (*Compt. rend.*, 1920, **171**, 360—363).—Ordinary country rain water does not dissolve even traces of copper from the precipitate obtained in either Bordeaux or Burgundy mixtures.

W. G.

**Acidity of Japanese Acid Clay.** KIUHEI KOBAYASHI (*J. Chem. Ind. Japan*, 1920, **23**, 543—549).—Japanese acid clay (Japanese fuller's earth) is a closely related mixture of colloidal hydrous aluminium silicates,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$ , and an amorphous anhydrous compound of orthosilicic acid,  $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ , and may be expressed by the formula  $\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot x\text{H}_2\text{O}$ , where  $x$  is more than 6. The clay itself is not a true acid substance, and the acidity is to be ascribed to its adsorptive property. Adding an acid clay to some basic dye solution,  $\text{RCl}$ , it may be supposed that the so-called Helmholtz double layer is formed on the surface of the clay, and that it adsorbs hydroxyl ions in accordance with its properties as an acid gel, whilst hydrogen ions are liberated. The radicle R combines with the hydroxyl ions and the hydrogen ions unite with chlorine ions of the basic dye; hydrochloric acid will therefore be liberated. Reaction between an acid clay and neutral potassium chloride solution similarly produces hydrochloric acid, which dissolves aluminium in the clay. The aluminium chloride thus formed will be decomposed by hydrolysis into aluminium hydroxide and hydrochloric acid.

K. K.

**The Occurrence and Nature of the Plant Growth-promoting Substances in various Organic Manurial Composts.** FLORENCE ANNIE MOCKERIDGE (*Biochem. J.*, 1920, **14**, 432—450).—The ordinary organic manures used in horticultural and agricultural operations, namely, leaf-mould and fresh and well-rotted stable manure, and well-manured fertile soil, contain, in varying proportions, water-soluble substances, which are effective as plant growth-promoting substances, as is shown by the effect of their aqueous extracts on the development of plants of *Lemna major*. In all cases, the extract of rotted manure was more effective than that of the fresh material. All these materials contain appreciable quantities of nucleic acid and its derivatives in various stages of decomposition, and the greater the bacterial decomposition of the material concerned, the greater is the resolution of the original nucleic acid into its free bases.

W. G.

## Organic Chemistry.

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**Oxidation of Hydrocarbons by Oxygen. Oxidation of Paraffin.** C. KELBER (*Ber.*, 1920, 53, [B], 1567—1577. Compare Fischer and Schneider, this vol., i, 519; Grün, this vol., i, 520).—In a previous communication (this vol., i, 280), the author has dealt with the volatile acids obtained by the oxidation of paraffin; he now describes the investigation of the residual mass, which amounts to 90—100% of the initial material, and has iodine number 1—2, saponification number 250—300, and acid number about 200. The highly complex mixture of acids cannot be separated into its components by the ordinary methods, and only by a suitable combined process is it possible to isolate and identify certain acids. At present, efforts have been mainly directed towards the characterisation of solid, saturated, normal fatty acids from  $C_{10}H_{20}O_2$  onwards, such as occur in the animal and vegetable organisms.

The crude residue is washed with water and then hydrolysed with alkali hydroxide; after removal of unsaponifiable matter, the acids are liberated, and a fraction soluble in light petroleum is prepared. This fraction is esterified with ethyl alcohol, and a partial separation is effected by distillation of the ethyl esters under diminished pressure. The ester fractions are separately hydrolysed, and the resulting acids are separated by suitable combinations of the following methods: (i) crystallisation of the acids, (ii) separation of the potassium salts by acetone (compare Fuchini and Dorta, A., 1914, ii, 153), (iii) the magnesium acetate method, and (iv) crystallisation of a mixture containing a suspected acid from a saturated solution of that acid. The presence of the following acids has so far been established: decoic, myristic, palmitic, heptadecic, stearic, and arachidic, and an acid,  $C_{16}H_{32}O_2$ , which is isomeric with palmitic and possibly identical with Bergmann's isopalmitic acid (A., 1918, i, 285).  
H. W.

**The Chlorination of Ethylene in the Presence of Calcium Chloride.** J. A. SMYTHE (*Gas J.*, 1920, 149, 691—693).—A simple apparatus is described for use with Newth's method (T., 1901, 79, 915) for the preparation of ethylene, by means of which a steady supply of the pure gas may be obtained. When the gas prepared in this way is passed, along with chlorine, over a short layer of calcium chloride in a water-cooled tube, a mixture of dichloroethane (50%), trichloroethane (25%), and less volatile compounds (25%) is obtained, and from this pure dichloroethane may readily be separated by fractionation. The trichloroethane probably results from the secondary action of chlorine on the dichloroethane, and not from the preliminary formation of vinyl chloride with subsequent addition of chlorine. The less volatile compounds are probably chloro-derivatives of polymerides of ethylene.

Dichloroethane behaves towards potassium carbonate in a precisely similar manner to dibromoethane, giving ethylene glycol and vinyl chloride, but the action is much slower than with the dibromoethane.

W. G.

**The Interaction of Ethylene and Sulphuryl Chloride.** WILLIAM FOSTER (*Science*, 1920, **51**, 641—642).—At the ordinary temperature, no apparent change occurs when ethylene is bubbled through sulphuryl chloride. Under certain conditions, not mentioned, on continued passage of the gas the solution becomes greenish-yellow, and the temperature rises to a maximum of 35—40°. Then the solution becomes colourless, the temperature falls, and the colour reappears. This cycle is repeated often, each time becoming longer and the temperature differences less pronounced. Some products of the reaction are ethylene dichloride and sulphur dioxide. The subject is still under investigation.

CHEMICAL ABSTRACTS.

**Preparation and Characterisation of Ethylenebromohydrin.** JOHN READ and REXFORD GEORGE HOOK (*T.*, 1920, **117**, 1214—1226).

**Preparation of *iso* Amyl Alcohol by Pasteur's Method.** FÉLIX MARTIN (*J. Pharm. Chim.*, 1920, [vii], **22**, 220—226).—In the preparation of the amylsulphuric acids, which is the first step in the isolation of pure *iso* amyl alcohol from fusel oil by the fractional crystallisation of the barium amylsulphates, the best results are obtained with 90—91% sulphuric acid (D 1.820—1.825), using an excess of 15—20% above the theoretical quantity. Under these conditions, about 60% of the alcohol is esterified, but as a small proportion is apparently converted into the normal sulphate, the actual yield of the acid sulphates amounts to about 50—55%. If a large excess of sulphuric acid is used, considerable difficulties are encountered later in the separation of the barium sulphate without any adequate compensation in the increased percentage of alcohol esterified.

G. F. M.

**[Reactions and Derivatives of  $\beta\beta$ -Dichlorodiethyl Sulphide.]** O. B. HELFRICH (*J. Amer. Chem. Soc.*, 1920, **42**, 1839).—The author states that certain of the physical constants (this vol., i, 525) previously given are incorrect. The following are the corrected values: Line 24,\* read "b. p. 222—223°/21 mm." Line 20,\* "m. p. 171°." Line 17,\* "b. p. 173—175°/21 mm." Line 13,\* "b. p. 193—195°/22 mm."

W. G.

**Catalytic Reduction of Organic Compounds with the Aid of Nickel Carbonyl.** RUDOLF LESSING (D.R.-P. 321938; from *Chem. Zentr.*, 1920, iv, 367).—(1) The catalyst is brought into action at the moment of decomposition of the nickel carbonyl. (2) The nickel carbonyl and hydrogen or gases, which are richer in hydrogen than technical water-gas, are brought into contact with the substance to be hydrogenated at a suitable temperature

\* From bottom.

during the whole course of hydrogenation. (3) The nickel carbonyl is dissolved in the substance under treatment, and the solution is injected into a heated vessel, in which it comes into contact with hydrogen or the hydrogenating agent.

Hydrogen containing 5—10% of carbon monoxide is used in the treatment of oils or fatty acids. The more volatile tar oils, benzene, etc., are heated to the requisite temperature with hydrogen containing nickel carbonyl; the preparation of aniline from nitrobenzene is effected similarly. H. W.

**Keto-enolic Desmotropy. XII. The Fractional Distillation of Ethyl Acetoacetate.** KURT H. MEYER and VIKTOR SCHOELLER (*Ber.*, 1920, 53, [B], 1410—1416).—Ethyl acetoacetate has been distilled from a Jena-glass apparatus which had been cleaned by being steamed, washed with alcoholic hydrogen chloride, and dried at 100°. The operation was performed under 2 mm. pressure, and the ester was thus divided into four equal fractions and a residue in the flask; the former contained 78%, 76%, 72%, and 63%, respectively, of the enolic form, of which only 5% was present in the residue. The whole distillate is highly enolised, whilst an ester richer in the ketonic form remains in the flask. Special experiments show that enolisation only occurs to a slight extent in the vaporous phase, even when this is superheated and in contact with glass. The change seems to be mainly located on the walls of the neck of the flask and the column, where the condensed ketone, in boiling, is isomerised to the equilibrium ester, which evolves the more volatile enolic form. Since the desmotropic change was probably due to the catalytic action of the glass, the experiment was repeated, using a quartz flask with glass condenser and receivers; the enolic contents of three fractions and a residue, all of equal volume, were 22, 11, 2.5, and 0% respectively. The mean percentage of enol in distillates and residue combined was 8.9%, so that the ester was practically unaffected by the distillation. It appears beyond doubt that fractionation under "aseptic" conditions affords the readiest means of isolating the pure ketone, and the enolic form may also be isolated by repeated distillation of larger amounts. (The enolic content of the various fractions is deduced from their refractive indices, a graph showing the relationship between the two functions being given in the original.)

Methyl benzoylacetate has been similarly distilled from a glass flask; three successive fractions contained 40, 21, and 20% of the enolic form, which was present to the extent of 8% in the residue and 18% in the original ester. In this experiment, it is noteworthy that the first drops of the distillate solidified in the condenser, a sign of the presence of the almost pure enolic form. H. W.

**Decomposition of the Acid Salts of Dibasic Acids in Aqueous Solution. V.** TH. SABALITSCHKA (*Ber.*, 1920, 53, [B], 1383—1387. Compare A., 1919, i, 433, and previous abstracts).—Aqueous solutions of the potassium hydrogen salts of malonic,

succinic, maleic, and fumaric acids have been extracted with ether, and the amount of acid removed has been determined; the partition-coefficient of the free acids between ether and water has been measured under identical conditions. The ethereal solution was found to contain about one-thirteenth of the malonic acid originally present in the acid salt, whilst the corresponding fractions for succinic and fumaric acids are one-sixth and one-fifth; further, the presence of free acid in the aqueous solution of the hydrogen maleate could not be detected. Protracted continuous extraction of an aqueous solution of potassium hydrogen succinate by ether showed that it is possible to remove nearly the whole of the acid portion by this means, but the process becomes very slow towards the end, partly by reason of the diminished concentration of the free acid in the aqueous solution, but also in consequence of the presence of relatively large quantities of normal salt. H. W.

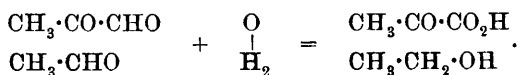
**The Electrosynthetic Preparation of *n*-Tetradecane- $\alpha\omega$ -dicarboxylic Acid.** KARL STOSIUS and KARL WIESLER (*Biochem. Zeitsch.*, 1920, **108**, 75—81).—On electrolysing the potassium ethyl ester of azelaic acid, ethyl *n*-tetradecane- $\alpha\omega$ -dicarboxylate was obtained:  $2\text{CO}_2\text{Et}\cdot[\text{CH}_2]_7\cdot\text{CO}_2\text{K} = \text{CO}_2\text{Et}\cdot[\text{CH}_2]_{14}\cdot\text{CO}_2\text{Et} + 2\text{CO}_2 + 2\text{K}$ . From this the acid was obtained, and found, as expected, to be identical with thapsic acid, isolated by Canzoneri from juniper berries (A., 1884, 461). S. S. Z.

**The Growth of Crystals of Potassium Sodium Tartrate.** MISHIO ISHIMOTO (*Proc. Phys.-Math. Soc. Japan*, 1920, [3], **2**, 81).—The crystals of potassium sodium tartrate were obtained from the solution by very slow cooling. Successful growth depends on the rate of cooling and the evaporation of the liquid. The solution was kept in a 25-litre thermostat heated electrically. The vessel containing the solution was sealed practically air-tight to retard the evaporation of the liquid. The solution was prepared to be saturated at a temperature between 30° and 32°, and its rate of cooling was slow, about 0.2—0.4° per day. In such a way, crystals of 6—7 cm. in length were obtained in two weeks or more. CHEMICAL ABSTRACTS.

**Production of Saccharic Acid and Tartaric Acid from Carbohydrates.** DIAMALT AKT.-GES. (Brit. Pat. 108494).—Saccharic and tartaric acids are readily obtained by oxidising carbohydrates with sulphuric and nitric acids, or sulphuric acid and oxides of nitrogen, peroxidised by treatment with air, ozone, or oxygen, at a temperature of 100°, in presence of oxidising catalysts, particularly molybdenum, mercury, or platinum. For example, 100 parts of starch are mixed with 150 parts of water and 3 parts of sulphuric acid and saccharified. Concentrated sulphuric acid (25 parts), nitric acid (D 1.4; 60 parts), and an oxide of molybdenum (1 part) are then added, and the reaction mixture is maintained at 100°, a further 100—140 parts of nitric

acid being gradually introduced. At the end of the operation, the nitric acid is evaporated, and, after diluting the residual liquor with water, the molybdenum is precipitated by hydrogen sulphide and the sulphuric acid and traces of oxalic acid by lime or baryta, and saccharic acid separated from the filtrate, after concentration, as potassium hydrogen saccharate. The yield amounts to 65%. If mercury is used as catalyst, and twice the quantity of nitric acid is added, a yield of 60% of potassium hydrogen tartrate, together with about 10% of saccharate, is obtained. G. F. M.

**Mixed Dismutation of Aldehydes.** F. F. NORD (*Biochem. Zeitsch.*, 1920, **106**, 275—280).—The reaction between two different aldehydes, expressed by the equations  $R \cdot CHO + R_1 \cdot CHO + H_2O = R \cdot CH_2 \cdot OH + R_1 \cdot CO_2H$  or  $R_1 \cdot CH_2 \cdot OH + R \cdot CO_2H$ , is termed mixed dismutation of aldehydes. According to Neuberg's theory of fermentation (Neuberg and Kerb, A., 1914, i, 118), such a reaction may be assumed to take place between the two intermediate products, methylglyoxal and acetaldehyde, in such a way that pyruvic acid and ethyl alcohol are formed until all the sugar is exhausted:

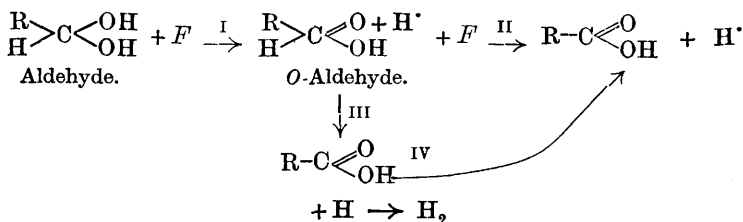


The author has investigated the reactions between the following pairs of aldehydes in presence of aluminium ethoxide as condensing agent: (1) acetaldehyde and *isovaleraldehyde*, (2) *isovaleraldehyde* and benzaldehyde, and (3) acetaldehyde and benzaldehyde. In each case, mixed dismutation occurs, the products in case (1), for instance, being ethyl acetate, amyl valerate, amyl acetate, and ethyl valerate. T. H. P.

**The Dehydroxidation of Aldehydes. Mechanism of Oxidation.** ERICH MÜLLER (*Annalen*, 1920, **420**, 241—261. Compare Müller and Hochstetter, A., 1914, ii, 615; Fichter, A., 1918, ii, 439).—It has been shown that when an alkaline solution of formaldehyde is electrolysed with a copper anode, equal volumes of hydrogen are initially evolved from either pole, but the evolution from the anode gradually ceases as the electrolysis proceeds; it is now found that the process occurs for an indefinite period when the anode is made of copper foil which has been covered with molten cuprous chloride and subsequently cathodically reduced in sodium hydroxide solution, or of silver foil which has been treated in a similar manner. A similar action takes place in the presence of certain metallic oxides, of which cuprous and cupric oxides, as well as silver oxide, have been particularly investigated; in these cases there is a period of incubation. The reaction has been extended to acetaldehyde and benzaldehyde, which are also found to be converted into the corresponding acid and gaseous hydrogen. The latter is also evolved in small quantity from alkaline solutions of formaldehyde in the presence of certain metals and in the

absence of particular oxidising agents; these metals also catalytically accelerate the Cannizzaro reaction.

The mechanism of oxidation is represented by the following scheme:



in which  $F$  is the charge induced by the electric current or by an oxidising agent. The primary product of the oxidation of an aldehyde is the corresponding *O*-aldehyde; dehydroxidation occurs if this is more readily oxidised according to III than in accordance with II. Conversion of aldehyde into acid without evolution of hydrogen may occur along the lines I and II, or I, III, and IV. Whether or not hydrogen is evolved during the oxidation of the aldehyde in the presence of catalysts depends on whether the latter accelerate III more than IV. H. W.

### Quantitative Investigation of Cannizzaro's Reaction in the Condensation of Acetaldehyde by Aqueous Alkalis.

HARALD HAMMARSTEN (*Annalen*, 1920, **420**, 262—275).—The investigation forms part of a biochemical study of the function of acetaldehyde in plants. Under the action of aqueous alkali, the aldehyde is decomposed into alcohol and acid, into aldol and aldehyde resin. The first and third types of action are chiefly described in the present communication.

The experiments were carried out with *N*/2-aqueous acetaldehyde solution at 0°, 18°, and 50° respectively. The bases used were the hydroxides of potassium, barium, calcium, and lead. In addition, buffer solutions prepared from the di- and mono-hydrogen phosphates of potassium and sodium, and from borate and sodium hydroxide, were also employed. In the case of the alkali hydroxide solutions, the amount of acid formed was estimated by titration of the resulting solution with acid in the presence of phenolphthalein; with the buffer mixtures, the solutions were strongly acidified with phosphoric acid, distilled to syrupy consistency, and subsequently treated with steam until all acetic acid was removed, the latter being then titrated in the combined distillate. Aldehyde resin was estimated by extraction of the solutions with chloroform, evaporation of the latter, and desiccation of the residue at 120°/10 mm. until constant in weight.

The results are given in an extended series of tables. It is found that the aldol condensation proceeds at a relatively much greater rate than the Cannizzaro reaction, the former taking place

so rapidly that it is impossible for any considerable amounts of alcohol or acid to be formed. The maximum production of acid observed during the whole course of the experiments is only 12·5% of that theoretically possible. H. W.

**Additive Compounds of the Acetylacetone Derivatives of the Rare Earths.** G. JANTSCH and E. MEYER (*Ber.*, 1920, 53, [B], 1577—1587. Compare Biltz and Clinch, A., 1904, i, 715.)—A series of additive compounds of the acetylacetone derivatives of the rare earths with ammonia, aniline, and pyridine has been investigated in the hope that a convenient chemical means of separating these elements might be found in their internally complex salts or their additive compounds. This does not, however, appear to be the case. The compounds which are described are considered to be constituted according to the annexed general formula.

$$\left[ M \left( \begin{array}{c} \text{O} \cdot \text{CMe} \\ \text{>CH} \\ \text{O} \cdot \text{CMe} \end{array} \right) \right] \dots R$$
 Lanthanum acetylacetone, m. p. 151° (Biltz, *loc. cit.*, gives 183°), combines with a molecule of ammonia, pyridine, or aniline, respectively, to yield *compounds*, colourless needles, m. p. 147·5°, slender, colourless needles, m. p. 142°, and colourless, silky needles, m. p. 192°. *Lanthanum dibenzoylmethane*, pale yellow, shining needles, m. p. 141—143°, is obtained by the action of dibenzoylmethane on a suspension of lanthanum hydroxide in boiling ethyl alcohol; it combines with a molecule of ammonia, yielding a *substance*, pale yellow, slender needles, m. p. 99°, which rapidly loses the whole of the ammonia on exposure to air. Gadolinium acetylacetone is isolated in the form of the *dihydrate*, which, when crystallised from absolute alcohol, passes into the *monohydrate*, colourless, transparent needles, m. p. 142°; the *pyridine* compound,  $\text{Gd}(\text{C}_5\text{H}_7\text{O}_2)_3 \cdot \text{C}_5\text{H}_5\text{N}$ , forms colourless needles, m. p. 139·5°. *Yttrium acetylacetone*, colourless, transparent, pointed needles, m. p. 131°, is prepared in the same manner as the lanthanum salt, than which it is considerably more stable; the *compounds* with ammonia, pyridine, aniline, and acetonitrile form colourless needles, m. p. 129°, slender, shining needles, m. p. 121°, small needles, m. p. 109°, and colourless, fatty crystals, m. p. 138°; the first- and last-named compounds are somewhat unstable. *Yttrium dibenzoylmethane* forms long, yellow, shining needles, m. p. 240°; it does not appear to yield additive compounds with ammonia, pyridine, aniline, or acetonitrile. H. W.

**Mutarotation of Dextrose in Alkaline Solution.** HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1920, 106, 23—36).—The author has measured the velocities of disappearance of the mutarotation of dextrose in distilled water and in *N*/10—*N*/7000-sodium carbonate solutions, all the measurements being carried out at 20·4°. The values of the velocity constant of the change of mutarotation for different concentrations of sodium carbonate are: water, 7·11; *N*/7000, 7·32; *N*/6000, 9·32; *N*/5000, 12·70;



$N/2000$ , 24.4;  $N/1000$ , 56.5;  $N/500$ , 93.1, these numbers giving almost exactly a straight line when plotted against the concentrations of the alkali (compare Osaka, A., 1909, i, 456).

T. H. P.

**The Stability of  $\alpha$ -Dextrose.** HANS VON EULER and ARVID HEDELIUS (*Biochem. Zeitsch.*, 1920, **107**, 150—158).—The H-ion concentration conducive to the maximum stability in the mutarotation of dextrose is  $P_H = 3.6 \pm 0.2$ . The temperature-coefficient at this H-ion concentration is only slightly higher than that at  $P_H = 5$ .

S. S. Z.

**Action of the Carbonates of the Alkaline Earths on Dextrose. III.** HANS MURSCHAUSER (*Biochem. Zeitsch.*, 1919, **101**, 74—81. Compare this vol., i, 13, 662).—As in the case of calcium carbonate, strontium carbonate, barium carbonate, and magnesium carbonate when boiled with a solution of dextrose, gradually reduce the dextrorotation of the solution to zero or to slight levorotation. The reduction of the sugar also falls, but to a smaller extent than the rotation. The formation of levulose is established by the isolation of the phenylmethylosazone of this sugar from the treated solution. The fall in the reduction is ascribed to the formation of acids. The velocity of the change in the rotation is proportional to the equivalent weights of the dissolved substances.

S. S. Z.

**Rate of Hydrolysis of Phosphoric Esters of Sugar Derivatives.** P. A. LEVENE and M. YAMAGAWA (*J. Biol. Chem.*, 1920, **43**, 323—338).—There is much evidence that the ester derivatives of sugar may show considerable differences in the rate at which they are hydrolysed. The substances studied in this work were the phosphoric esters of (1)  $\alpha$ -methylglucoside; (2)  $\beta$ - $\gamma$ -trimethyl methylglucoside; (3)  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\epsilon$ -diacetone-glucose; (4)  $\alpha\beta$ -monoacetone-glucose; (5) a phosphoric acid ester of the same sugar derivative as in (4), but differing in the position of the acid radicle; (6)  $\zeta$ -benzoyl- $\alpha\beta$ -monoacetone-glucose. The position of the phosphoric acid in the first compound is not known, but in (2) and (3) it is attached to the same carbon atom, so that these two compounds differ only in the nature of the substituent group. The fourth substance is formed as a by-product by the action of phosphoryl chloride on diacetone-glucose, and apparently contains the phosphoric acid radicle attached to a primary alcohol grouping, whereas the fifth substance is prepared by the action of phosphoryl chloride on monoacetone-glucose, and contains the phosphoric acid linked to a secondary alcohol group. The sixth substance differs from the preceding two by containing the phosphoric acid in a different position, by the number of the substituting groups, and by the difference in character of one of these groups.

The hydrolysis of these six substances was studied in approximately equivalent concentration, which was in the neighbourhood of

10%. The condition of hydrolysis consisted of treatment with 0.1*N*-sulphuric acid at 100°. The rate of hydrolysis followed the unimolecular law, and the following constants were obtained:  $K_1$ , 22(10<sup>-3</sup>);  $K_2$ , 43(10<sup>-3</sup>);  $K_3$ , 56(10<sup>-3</sup>);  $K_4$ , 44(10<sup>-3</sup>);  $K_5$ , 58(10<sup>-3</sup>);  $K_6$ , 18(10<sup>-3</sup>).

These results indicate that both the position of the phosphoric acid radicle and the character of the substituent groups exert an influence on the stability of the ester linking. J. C. D.

**Crystalline Chlorotetra-acetyllævulose and Related Derivatives.** D. H. BRAUNS (*J. Amer. Chem. Soc.*, 1920, **42**, 1846—1854).— $\beta$ -Penta-acetyllævulose, when shaken in chloroform solution with aluminium chloride and phosphorus pentachloride, gives *chlorotetra-acetyllaevulose*, m. p. 83°,  $[\alpha]_D^{20}$  -160.9°, which slowly decomposes in the air, giving tetra-acetyllævulose. By its general behaviour it is probable that this compound is an  $\alpha$ -derivative. A better yield of the compound is obtained if the tetra-acetate is used instead of the penta-acetate, whilst if aluminium chloride is omitted in the preparation, the main product is  $\beta$ -*chlorotetra-acetyllaevulose*, m. p. 108°,  $[\alpha]_D^{20}$  +45.3°. On ethylation, tetra-acetyllævulose gives  $\beta$ -*ethyltetra-acetyllaevulose*, m. p. 83°,  $[\alpha]_D^{20}$  -127.6°.  $\beta$ -*Ethyl laevuloside*, m. p. 151°,  $[\alpha]_D^{20}$  -155.3°, was obtained by the process previously described for  $\beta$ -methyl laevuloside (compare A., 1916, i, 547). Attempts to prepare  $\alpha$ -methyl laevuloside by a biochemical method or by Fischer's method (compare A., 1895, ii, 553) were not successful. W. G.

**Action of Different Catalysts on the Combustion of Burning Sucrose.** J. ARVID HEDVALL (*Svensk. Kem. Tidskr.*, 1920, **32**, 99—103; from *Chem. Zentr.*, 1920, iii, 337—338).—The author has extended the observations of Schade (*Münch. med. Woch.*, 1905, i, 1088) on the combustion of pieces of sucrose in air by distinguishing between the burning without formation of residue and that with the production of a porous mass, and by examining the effect of a large number of catalysts. The type of combustion first named is caused by strongly basic oxides and hydroxides, by certain oxides which are known to form complex organic compounds or to yield higher oxides transitorily, and by certain free metals. The formation of a residue occurs in the presence of free halogens, halogen hydracids, sulphuric acid, and certain other acids, and of many normal salts. H. W.

**The Chemistry of Polysaccharides. The Preparation of Pure Polysaccharides. The Mode of Action of Diastatic Enzymes and the Dextrin Stage of Polysaccharides.** E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1920, **107**, 268—294).—Pure starch was prepared by digesting fresh plant tissue with 33% sodium hydroxide on the water-bath, and by precipitating with 90% alcohol after centrifuging off the insoluble constituents. The precipitate was dissolved in water and repre-

cipitated with 90% alcohol, this being repeated twice; it was finally neutralised with hydrochloric acid, and precipitated again with alcohol. The same method was employed in the treatment of yeast, and the insoluble portion obtained by centrifuging the product from the first digestion of the yeast with the alkali was treated again with boiling alkali and alcohol, which yielded a cellulose-like substance. Cellulose was prepared from cotton wool by digesting it with strong sodium hydroxide and small quantities of carbon disulphide, centrifuging, and precipitating the viscous fluid with 90% alcohol. It was purified by reprecipitation with alcohol and neutralised with hydrochloric acid. Agar was purified by precipitating an alkaline solution of it with alcohol. Glycogen was obtained by digesting minced liver with 33% sodium hydroxide, and was purified by precipitation with alcohol. The properties of the polysaccharides prepared by the above methods were studied. The theory of the iodine reaction and of the action of diastatic enzymes as explained from considerations of the condition of the dispersed colloidal particles of the polysaccharides is discussed.

S. S. Z.

**A Compound of Starch with Phosphoric Acid.** JOHANNES KERB (*Biochem. Zeitsch.*, 1919, **100**, 3—14).—Starch was esterified with phosphoric acid by treating a soluble preparation with a solution of phosphoryl chloride in chloroform in the presence of calcium carbonate. The calcium salt of the amylophosphoric acid was precipitated with alcohol from the concentrated solution and purified. By means of diastatic cleavage, hexose monophosphoric acid was obtained from the compound in the form of a calcium salt. The latter substance was fermented by yeast. S. S. Z.

**Preparation and Properties of a Highly-oxidised Cellulose.** EDMUND KNECHT and LEONARD THOMPSON (*J. Soc. Dyers and Col.*, 1920, **36**, 251—255).—An improved method for preparing oxycellulose is carried out by treating filter paper with an acid solution of potassium permanganate (either one or two atoms of oxygen for each molecule of cellulose— $C_6H_{10}O_5$ ), washing the brown, disintegrated powder so formed, decolorising with hydrogen peroxide, and drying at 40°. In the stronger oxidation, the aldehyde group in the oxycellulose is not attacked. The method avoids the decomposition of oxycellulose by alkalis into non-reducing substances and its hydrolysis by acids. The so-formed oxycellulose gives an intense yellow colour with sodium hydroxide, and, on neutralisation, an acid cellulose having only slight reducing power is formed. It forms hydrazones with phenylhydrazine and *p*-nitrophenylhydrazine. On reduction, oxycellulose does not yield cellulose.

When kept for one day with cold 0.880 ammonia solution, a gelatinous mass is formed, which retains various amounts of ammonia on washing. Probably an unstable aldehyde-ammonia is formed. Oxycellulose does not react with aniline, but with hydrazine hydrate, hydroxylamine, and hydrogen cyanide it gives

indefinite compounds containing nitrogen. It reacts with sodium hydrogen sulphite solution.

Oxycellulose exerts its strongest reducing power in alkaline solution, and reduces solutions of cupric, silver and ferric salts. In the presence of sodium hydroxide, it readily reduces methylene-blue, safranine, rosinduline, indanthren, and indigotin.

It is not possible to estimate oxycellulose by means of its reaction with *p*-nitrophenylhydrazine, since absorption compounds are formed.

The new oxycellulose had a copper number of 14.2, as compared with 7.6 for Nastjukov's bleaching powder-oxycellulose.

A. J. H.

### Picrates of the Nitrogen Bases of the Alcohol Radicles.

A. RIES (*Zeitsch. Kryst. Min.*, 1920, **55**, 454—522. Compare T., 1909, **95**, 1275.)—Detailed crystallographic and optical data are given for thirty-one compounds, ranging from methylammonium picrate to tetra-*n*-propylammonium picrate. Many are dimorphous or trimorphous, whilst trimethylisopropylammonium picrate is tetramorphous, and trimethylisobutylammonium picrate is pentamorphous, namely, (1) monoclinic,  $D^{15}$  1.378; (2) triclinic,  $D^{15}$  1.378; (3) monoclinic-domatic,  $D^{15}$  1.419; (4) triclinic, probably asymmetric,  $D^{15}$  1.377; (5) hexagonal,  $D^{15}$  1.377. Many are hexagonal or pseudo-hexagonal, or with prism-angles approaching  $60^\circ$ .

L. J. S.

### Certain New Transformations of Ethylenediamine.

WILHELM TRAUBE and ELISABETH PEISER (*Ber.*, 1920, **53**, [B], 1501—1508).—Aminoethylaminosulphonic acid (Traube and Brehmer, A., 1919, i, 434) has been converted into the corresponding nitroso-derivative, by the decomposition of which a series of hydroxy-, alkyloxy-, and halogeno-ethylamines has been prepared.

A well-cooled solution of  $\beta$ -aminoethylaminosulphonic acid in water is mixed with an aqueous solution of sodium nitrite, and subsequently acidified with dilute sulphuric acid, when  $\beta$ -aminoethylnitrosoaminosulphonic acid,  $C_2H_4 \begin{matrix} \text{---NH}_3\text{---} \\ \text{N(NO)SO}_3 \end{matrix}$ , separates in well-defined crystals, which are extremely explosive when dry (the moist preparations are used in the following experiments). The acid decomposes quantitatively in boiling aqueous solution in accordance with the equation  $NH_2 \cdot CH_2 \cdot CH_2 \cdot N(NO) \cdot SO_3H + H_2O = NH_2 \cdot CH_2 \cdot CH_2 \cdot OH + N_2 + H_2SO_4$ , and the  $\beta$ -aminoethyl alcohol was identified as the picrate, m. p.  $159^\circ$ , and picrolonate, m. p.  $225^\circ$  (decomp.). Concentrated hydrochloric acid converts the nitroso-acid into  $\beta$ -chloroethylamine (the sulphate was analysed), whilst hydrobromic acid acts with such violence that explosions readily occur, and gives  $\beta$ -bromoethylamine.  $\beta$ -Fluoroethylamine, obtained by treatment of the nitroso-acid with 40% hydrofluoric acid, evaporation of the solution, and distillation of the residue with steam after addition of an excess of alkali, has a strong odour

of ammonia, and is distinguished from the remaining halogenoethylamines by the much greater firmness with which the halogen atom is retained. The *hydrochloride*, *hydrobromide*, and *nitrate* are crystalline salts, but are not very characteristic by reason of their hygroscopic nature and ready solubility; the *picrolonate* crystallises in yellow, non-hygroscopic needles, m. p. 239°.

*β-Aminoethyl methyl ether*, colourless, mobile liquid, b. p. 95°/756 mm., is prepared from the nitroso-acid and boiling absolute methyl alcohol; the *hydrochloride*, hygroscopic crystals, and the *picrolonate*, yellow needles, m. p. 235°, are described. *β-Amino-diethyl ether* (picrolonate, m. p. 204°) is prepared in a similar manner. *β-Aminoethyl methyl ether hydrochloride* is transformed by potassium cyanate solution into *β-carbamidoethyl methyl ether*,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OMe}$ , m. p. 63° after softening at 61°. The aqueous solution of the base reacts with phenylcarbimide to give *phenylcarbamidoethyl methyl ether*, m. p. 94·5°. *β-Aminoethyl n-propyl ether* was isolated in the form of its *picrolonate*, yellow, prismatic crystals, m. p. 188°, when rapidly heated.

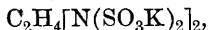
The action of phenol on *β-aminoethylnitrosoaminosulphonic acid* leads to the formation of *β-aminoethyl hydrogen sulphate* instead of the expected aminoethyl phenyl ether. H. W.

**Alkylimidodisulphonic Acids.** WILHELM TRAUBE and MAX WOLFF (*Ber.*, 1920, **53**, [B], 1493—1501).—The investigation of the alkylation of basic potassium hydroxylaminodisulphonate (Traube, Ohlendorf, and Zander, this vol., i, 717) has been extended to basic potassium imidodisulphonate,  $\text{NK}(\text{SO}_3\text{K})_2$ , which shows a somewhat similar behaviour, particularly towards the more active alkylating agents; with substances such as propyl iodide and benzyl chloride, the process is slower, the yields are poorer, and the products are mixed with potassium imidodisulphonate. The cause of this lies in the hydrolysis of the basic salt in aqueous solution,  $\text{NK}(\text{SO}_3\text{K})_2 + \text{H}_2\text{O} \rightleftharpoons \text{NH}(\text{SO}_3\text{K})_2 + \text{KOH}$ , and the dual nature of the process, which includes the alkylation of the basic salt and the decomposition of the alkyl haloid by free alkali; if the first process is slow and the second is comparatively rapid, equilibrium is so far disturbed by the removal of the alkali hydroxide that the normal salt is largely regenerated. Attempts to overcome this difficulty by working with concentrated solutions have not been particularly successful. The potassium alkylimidodisulphonates are readily decomposed by dilute acid into alkylamidodisulphonates, which are then slowly converted into the corresponding primary amines.

Basic potassium imidodisulphonate is readily transformed by methyl sulphate or methyl iodide into *potassium methylimidodisulphonate*,  $\text{NMe}(\text{SO}_3\text{K})_2$ , shining leaflets (the lead, silver, and barium salts dissolve freely in water), which is converted by very dilute sulphuric acid into *potassium methylamidodisulphonate*,  $\text{NHMe}\cdot\text{SO}_3\text{K}$ , and by 25% hydrochloric acid into methylamine hydrochloride, the yield of the latter being 88% of that theoretically possible. Similarly, *potassium ethylimidodisulphonate*, long

needles, is converted into ethylamine (yield, 64%) and *potassium propylimidodisulphonate*, long, shining needles, into propylamine (yield about 40%). *Potassium ephihydrinaminedisulphonate* is freely soluble in water.

*Potassium ethylenediamine-NN'-tetrasulphonate*,



small needles, is characterised by its sparing solubility in water, 100 c.c. of which dissolves only 0.2372 gram at the laboratory temperature (the *barium dipotassium* salt is practically insoluble in water). It is readily converted into *potassium ethylenediamine-NN'-disulphonate*, rectangular platelets, from which the corresponding free acid, shining leaflets, is obtained by means of perchloric acid, and, further, into ethylenediamine sulphate, the yield of the latter being 83% of that theoretically possible. H. W.

### A New Method for Producing Hexamethylenetetramine.

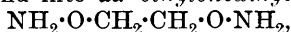
TH. SABALITSCHKA (*Zeitsch. angew. Chem.*, 1920, **33**, 217).—The formation of hexamethylenetetramine occurs, not only by the interaction of formaldehyde and free ammonia or ammonium carbonate, but also when a neutral ammonium salt, such as ammonium chloride, is employed in the absence of any alkali whatever. The quantitative aspect of the reaction in this case has not yet been investigated. G. F. M.

**The Preparation of  $\alpha$ -Derivatives of Hydroxylamine by means of Potassium Hydroxylaminedisulphonate.  $\alpha$ -Methylhydroxylamine and  $\alpha\alpha$ -Ethylenedihydroxylamine.** WILHELM TRAUBE, HEINRICH OHLENDORF, and HERBERT ZANDER (*Ber.*, 1920, **53**, [B], 1477—1492).—*Potassium  $\alpha$ -methylhydroxylamine- $\beta\beta$ -disulphonate*,  $\text{OMe}\cdot\text{N}(\text{SO}_3\text{K})_2$ , is readily obtained by shaking an aqueous solution of potassium hydroxylaminedisulphonate in the presence of that quantity of potassium hydroxide which is required to form the basic salt,  $\text{OK}\cdot\text{N}(\text{SO}_3\text{K})_2$ , with methyl iodide, or, more rapidly, with methyl sulphate (the corresponding *lead*, *barium*, and *silver* salts are freely soluble in water), and is converted by being heated for a moment with dilute sulphuric acid into  *$\alpha$ -methylhydroxylamine- $\beta$ -sulphonic acid*, hygroscopic syrup, which is most readily isolated in the form of its *potassium* salt, well-formed, pearly plates (the *barium* salt, long, transparent prisms,  $+1\text{H}_2\text{O}$ , was analysed; the *lead* and *silver* salts are freely soluble in water). Protracted action of boiling sulphuric or hydrochloric acid on potassium methylhydroxylaminedisulphonate causes the elimination of both sulphonic groups and the formation of  *$\alpha$ -methylhydroxylamine*, which is most readily isolated by adding an excess of alkali to the product of the action and distillation of the mixture with steam; the free base, b. p.  $49\text{--}50^\circ$ , is a colourless, mobile liquid with an amine-like odour. It reduces ammoniacal silver solution, but not Fehling's solution, at the ordinary temperature. The normal *sulphate*, m. p.  $144^\circ$ , the *nitrate*, large, transparent prisms, which detonate violently at

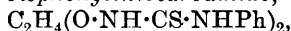
about 300°, and the *picrate*, m. p. 175°, are described. The base reacts with benzaldehyde to yield *anti-benzaldoxime O-methyl ether*, b. p. 191°, and with alloxan to give *methyl violurate*, m. p. 258—265°; it is converted by an aqueous solution of potassium cyanate into *methoxycarbamide*, m. p. 82—83°, by phenylthiocarbamide into *N-phenyl-N'-methoxythiocarbamide*, m. p. 116°, and by ethyl chloroformate into methoxyurethane, colourless oil, b. p. 186—188°. It combines with carbon disulphide to yield the very unstable salt,  $\text{OMe}\cdot\text{NH}_2\cdot\text{HS}\cdot\text{CS}\cdot\text{NH}\cdot\text{OMe}$ , which was analysed in the form of the corresponding *silver* compound,  $\text{C}_2\text{H}_3\text{ONS}_2\text{Ag}_2$ , intensely yellow precipitate, which decomposes above 40°.

*Potassium ethylhydroxylaminedisulphonate*, well-formed clusters of needles, is considerably more slowly formed from basic potassium hydroxylaminedisulphonate than is the corresponding methyl derivative, and is converted successively into *potassium ethylhydroxylaminemonosulphonate*, shining needles, readily soluble in water (the *free acid* is hygroscopic), and ethylhydroxylamine hydrochloride, m. p. 126°. Epichlorohydrin and the basic sulphonate yield *potassium epihydrinhydroxylaminedisulphonate*,

$\text{O} \begin{array}{c} \diagup \\ \text{CH}_2 \end{array} \text{CH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{N}(\text{SO}_3\text{K})_2$ , six-sided platelets. Similarly, ethylene dibromide gives *potassium  $\alpha\alpha'$ -ethylenedihydroxylamine-tetrasulphonate*,  $\text{C}_2\text{H}_4[\text{O}\cdot\text{N}(\text{SO}_3\text{K})_2]_2$ ; the corresponding *silver* and *lead* salts are freely soluble in water, but a mixed *potassium barium* salt dissolves more sparingly. The tetrasulphonate is transformed successively into the very soluble *potassium  $\alpha\alpha'$ -ethylenedihydroxylaminedisulphonate* and into  *$\alpha\alpha'$ -ethylenedihydroxylamine*,



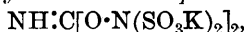
colourless liquid with a faint odour, b. p. 203°/atmospheric pressure (frequently accompanied by violent explosion), 105°/23 mm. It is only feebly alkaline in aqueous solution. The following derivatives are described: *sulphate*, m. p. 260°, which has an acid reaction in aqueous solution; *hydrochloride*, m. p. 233°; *nitrate*, m. p. 124°, which detonates when heated above its melting point; *biscarbamide*,  $\text{C}_2\text{H}_4(\text{O}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_2$ , colourless crystals, m. p. 190°; *bisphenylthiocarbamide*,



m. p. 119°.

Basic potassium hydroxylaminedisulphonate reacts comparatively rapidly with benzenesulphonyl chloride, *potassium benzenesulphohydroxylaminedisulphonate*,  $\text{SO}_2\text{Ph}\cdot\text{O}\cdot\text{N}(\text{SO}_3\text{K})_2$ , needles, moderately soluble in water being formed.

The action of cyanogen bromide or iodide on basic potassium hydroxylaminedisulphonate results in the formation of *potassium iminocarbonyldihydroxylaminetetrasulphonate*,



small needles (+ 2H<sub>2</sub>O); this salt is invariably produced when one molecular proportion of the cyanogen haloid is mixed with one or two molecular proportions of the salt, and appears to be formed by the condensation of a molecule of potassium cyanohydroxyl-

aminedisulphonate primarily produced with a further molecule of the basic salt.  
H. W.

**Action of Diazomethane on Amino-acids.** J. HERZIG and KARL LANDSTEINER (*Biochem. Zeitsch.*, 1920, **105**, 111—114).—The results of further experiments by Schuster (compare A., 1914, i, 753) show that Geake and Nierenstein's supposed proof of the betaine structure of the amino-acids (A., 1914, i, 1057) cannot be accepted as of general validity.

When glycine is treated with diazomethane, most of the former remains undissolved, the methoxyl value of the dissolved part being almost zero, and estimation of methylimide group giving a value only slightly above that obtained with glycine alone. Hippuric acid is converted mostly into the methyl ester. With alanine, which mostly remains undissolved, the soluble part contains 3.79% of methoxyl group. Phenylalanine and diazomethane yield an oil of the composition  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{NHMe})\cdot\text{CO}_2\text{Me}$ . These results and those obtained with leucine, glutamic acid, and tyrosine show that with only the two lowest amino-acids, glycine and alanine, diazomethane effects virtually no substitution, and that in either case introduction of a negative group into the molecule enhances the reactivity towards diazomethane. With the other amino-acids examined, a distinction must be made between substitution of the hydrogen of the carboxyl and amino-groups; substitution is almost complete in the former group, and takes place only with difficulty in the latter. The presence of free amino-acid is rendered probable by the reactivity of the carboxyl group, entry of the methyl residue at the nitrogen being possibly hindered by other unknown factors. According to Geake and Nierenstein's view, that absence of reactivity towards diazomethane in ethereal suspension constitutes a proof of the betaine structure of an amino-acid, such structure can be ascribed only to glycine and possibly to alanine, equilibrium between the betaine form and the ordinary form being assumed in other cases. The accuracy of Geake and Nierenstein's view is supported by the behaviour of glutamic acid.

T. H. P.

**Syntheses of  $\beta$ -Amino-acids from Substituted Ammonium Malonates and Formaldehyde.** C. MANNICH and B. KATHER (*Ber.*, 1920, **53**, [B], 1368—1371).—The action of formaldehyde on aqueous solutions of the salts of malonic acid and amines leads to the formation of  $\beta$ -amino-acids, in accordance with the equation

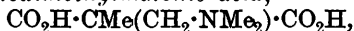
$$\text{CO}_2\text{H}\cdot\text{CHR}\cdot\text{CO}_2\text{H} + \text{NR}_2'/\text{H} + \text{CH}_2(\text{OH})_2 = \text{CO}_2\text{H}\cdot\text{CR}(\text{CH}_2\cdot\text{NR}_2')\cdot\text{CO}_2\text{H} + 2\text{H}_2\text{O}.$$

The reaction is most successfully applied to monoalkylmalonic acids and secondary amines, since, in this case, each component only contains one replaceable hydrogen atom, and action can only proceed in one direction. Malonic acid contains two and ammonia three hydrogen atoms, all of which can react with formaldehyde, so that the product of the change is too complex to permit the isola-



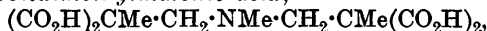
tion of individual substances. In the condensation, the nitrogen atom invariably occupies the  $\beta$ -position to the carboxyl group. The action of heat on the  $\beta$ -aminodibasic acid results, in general, in the loss of carbon dioxide and amine, and the formation of an unsaturated acid.

*$\omega$ -Dimethylaminodimethylmalonic acid,*



from methylmalonic acid, dimethylamine, and formaldehyde, forms small prisms, m. p. about  $98^\circ$  (decomp.), and is decomposed by heat into carbon dioxide, dimethylamine, and methylacrylic acid.

*Methyliminobisdimethylmalonic acid,*



decomposes, with evolution of gas, at  $83$ – $84^\circ$ , and cannot be preserved indefinitely at the ordinary temperature; it yields methylacrylic acid when heated.  *$\beta\beta'$ -Tetramethyldiaminoisobutyric acid* (from malonic acid, dimethylamine, and formaldehyde), needles, m. p.  $139^\circ$ , forms a *dihydrochloride*, slender needles, m. p.  $169^\circ$ , which gives a sparingly soluble double salt with mercuric chloride. Formaldehyde and methylammonium malonate yield a complex mixture, from which an *aurichloride*,  $\text{C}_5\text{H}_{10}\text{O}_2\text{NAuCl}_4$ , was isolated with difficulty.

H. W.

**The Preparation of Guanidine by the Interaction of Dicyanodiamide and Ammonium Thiocyanate.** EMIL ALPHONSE WERNER and JAMES BELL (T., 1920, 117, 1133–1136).

**Fixation of Labile, Hydrated Forms by means of Mercuric Cyanide.** G. SCAGLIARINI and E. BONINI (*Gazzetta*, 1920, 50, ii, 114–117).—Treatment of cobalt or nickel sulphate solution with mercuric cyanide solution yields the isomorphous double sulphates,  $\text{CoSO}_4 \cdot \text{Hg}(\text{CN})_2 \cdot 10\text{H}_2\text{O}$  and  $\text{NiSO}_4 \cdot \text{Hg}(\text{CN})_2 \cdot 10\text{H}_2\text{O}$ , the former orange-red and the latter greenish-blue. By similar procedure the salts,  $\text{Co}(\text{NO}_3)_2 \cdot \text{Hg}(\text{CN})_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2 \cdot \text{Hg}(\text{CN})_2 \cdot 6\text{H}_2\text{O}$ , may be obtained. When the complex cobalt sulphate is electrolysed in aqueous solution, the mercuric cyanide migrates to the cathode, and must hence be united, partly at least, to the cobalt atom (compare Kurnakov, A., 1898, ii, 475; Barbieri and Calzolari, A., 1911, i, 184, 266, 268).

T. H. P.

**Mercury Derivatives of Ethylene.** W. MANCHOT and ARTHUR KLÜG (*Annalen*, 1920, 420, 170–190).—The mercuriation of ethylene has been described by Hofmann and Sand in a series of communications during the years 1900 and 1901, as the final result of which they are led to consider that two types of substances are produced, to which they assign the formulæ  $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{HgX}$  and  $\text{X} \cdot \text{Hg} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{HgX}$  respectively. It has been shown, however, that the mercurated derivatives of acetylene are to be regarded as true acetylene derivatives (Manchot and Haas, A., 1913, i, 1009; Manchot and Mährlein, A., 1919, i, 145), and arguments are now advanced in favour of regarding the ethylenic compounds as additive substances,  $\text{C}_2\text{H}_4 \cdot \text{HgX} \cdot \text{OH}$  and  $2\text{C}_2\text{H}_4 \cdot \text{O}(\text{HgX})_2$ .

Hofmann and Sand's formula does not readily explain why their

compound is immediately decomposed by halogen acids with the violent evolution of acetylene, whereas it is stable towards other acids. According to the authors' experiments, a similar result is produced by the addition of potassium cyanide or potassium thiocyanate in the presence of acid. In general, the reaction is caused by all those substances which combine with mercuric haloids to yield additive compounds of the type  $\text{HgCl}_2 \cdot 2\text{HCl}$ , and may be expressed by the equations:  $\text{C}_2\text{H}_4 \cdot \text{OH} \cdot \text{HgCl} + \text{HCl} \rightleftharpoons \text{C}_2\text{H}_4 \cdot \text{HgCl}_2 + \text{H}_2\text{O}$  and  $\text{C}_2\text{H}_4 \cdot \text{HgCl}_2 + 2\text{HCl} \rightleftharpoons \text{HgCl}_2 \cdot 2\text{HCl} + \text{C}_2\text{H}_4$ . In support of this hypothesis, it is shown that compounds of the type  $\text{HgX}_2 \cdot 2\text{HX}$  can be isolated, although with some difficulty, and that the most characteristic substance of this class is  $\text{Hg}(\text{SCN})_2 \cdot 2\text{HSCN}$ , and further that aqueous solutions of mercuric chloride readily absorb ethylene with ultimate disappearance of the ionic reactions of mercury, and that the absorption is very much less marked when hydrochloric acid is added to the mercuric chloride solution. Further, as is to be expected from the equation  $\text{C}_2\text{H}_4 \cdot \text{OH} \cdot \text{HgCl} + \text{NaCl} \rightleftharpoons \text{C}_2\text{H}_4 \cdot \text{HgCl}_2 + \text{NaOH}$ , decomposition of the additive compound can be effected by the addition of alkali haloids, but, in consequence of the back action, the effect is not very marked, and is most noticeable when potassium thiocyanate is employed.

It has been observed previously by Sand that the complex,  $\text{C}_2\text{H}_4 \cdot \text{Hg}(\text{OH}) \cdot$ , behaves as a univalent radicle, and, in this connexion, the *dichromate*,  $[\text{C}_2\text{H}_4 \cdot \text{Hg}(\text{OH})]_2\text{Cr}_2\text{O}_7$ , has now been prepared. The free *base*,  $[\text{C}_2\text{H}_4 \cdot \text{Hg}(\text{OH})] \cdot \text{OH}$ , has also been isolated by the action of moist silver oxide on the corresponding bromide as a viscous mass which freely evolves ethylene on treatment with hydrochloric acid (the *platinichloride*,  $[\text{C}_2\text{H}_4 \cdot \text{Hg}(\text{OH})]_2\text{PtCl}_6 \cdot 5\text{H}_2\text{O}$ , was analysed). Contrary to the statement of Sand, the benzoyl derivative,  $\text{C}_2\text{H}_4 \cdot \text{Hg}(\text{OBz})\text{I}$ , evolves ethylene when treated with hydrochloric acid, the comparative slowness of the action being due to the insolubility of the substance.

The decomposition of mercurated ethylene compounds by iodine is readily explained by the additive formula; the primary action consists in the displacement of oxygen by iodine (which is in accordance with the well-known properties of mercury salts), followed by addition of oxygen at the double bond, thus yielding  $\text{CH}_2\text{I} \cdot \text{CH}_2 \cdot \text{OH}$  and  $\text{O}(\text{CH}_2 \cdot \text{CH}_2\text{I})_2$  respectively. The action of alkyl iodide lends further support to the additive hypothesis; according to Sand's formulation, the ethanol derivative,  $\text{HO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{HgI}$  should yield propyl alcohol when treated with methyl iodide, whereas it actually gives methyl alcohol, ethylene, and mercuric iodide. Similarly, the ethyl ether mercuri-salts yield ethylene in abundance when heated with methyl iodide at  $110^\circ$ ,  $2\text{C}_2\text{H}_4 \cdot \text{HgI} \cdot \text{O} \cdot \text{HgI} + 2\text{CH}_3\text{I} = 2\text{C}_2\text{H}_4 + 2\text{HgI}_2 + (\text{CH}_3)_2\text{O}$ .  
H. W.

**Relations between the Constitution and Physical Properties of Hydroaromatic Compounds.** K. VON AUWERS (*Annalen*, 1920, **420**, 84—111. Compare A., 1916, i, 130—131).—The present communication is mainly devoted to the *cyclohexanes*.

Since it is quite possible that stereoisomeric forms of these may be obtained according to the method of operation, they have in general been prepared according to a uniform scheme which starts from the requisite *cyclohexanol* obtained by Sabatier's method. The secondary *cyclohexanols* are converted into the iodides, and these are reduced to the hydrocarbons in accordance with Zelinski's method. The process is not readily applicable to tertiary *cyclohexanols*, since unsaturated hydrocarbons are readily produced; in these cases it is preferable first to transform them by phosphorus pentachloride into the chloro-compounds and to reduce the latter by sodium in the presence of moist ether, the latter operation being performed as slowly as possible. The products invariably contain small amounts of unsaturated hydrocarbons, which are removed by the addition of a slight excess of bromine followed by distillation in a vacuum. The products are ultimately distilled over sodium, and must finally neither show Beilstein's halogen test nor be coloured by tetranitromethane.

The validity of the rules governing the relation between constitution and physical properties which were propounded previously (*loc. cit.*) has been confirmed for a series of compounds, and certain apparent exceptions have been removed. Experiments directed to explain these exceptions have shown that the hydrogenation of benzene derivatives may lead to the formation of different stereoisomeric forms of the corresponding hydroaromatic derivatives when different methods are employed, and that with simple derivatives of *cyclohexane* the physical constants of stereoisomeric modifications may differ considerably.

The following compounds are described: 1:2-Dimethylcyclohexan-2-ol, b. p. 169°/ordinary pressure, 63—65°/9 mm.,  $D_4^{13.7}$  0.9252,  $D_4^{20}$  0.920,  $n_D^{13.7}$  1.46035,  $n_D^{13.7}$  1.46248,  $n_D^{13.7}$  1.46848,  $n_D^{13.7}$  1.47330,  $n_D^{20}$  1.4596; 2-chloro-1:2-dimethylcyclohexane, colourless oil, b. p. 53—54°/9 mm.,  $D_4^{13.3}$  0.9708,  $D_4^{20}$  0.965,  $n_D^{13.3}$  1.46492,  $n_D^{13.3}$  1.46723,  $n_D^{13.3}$  1.47407,  $n_D^{20}$  1.4642; 1:2-dimethylcyclohexane, b. p. 35—37°/23 mm., 122.5—123.5°/760 mm. (?),  $D_4^{17.85}$  0.7809,  $D_4^{20}$  0.779,  $n_D^{17.85}$  1.42820,  $n_D^{17.85}$  1.43020,  $n_D^{17.85}$  1.43592,  $n_D^{17.85}$  1.44056,  $n_D^{20}$  1.4292; 4-chloro-1:4-dimethylcyclohexane, b. p. 50.5—52°/14 mm.,  $D_4^{18.5}$  0.9438,  $D_4^{20}$  0.943,  $n_D^{18.5}$  1.45088,  $n_D^{18.5}$  1.45372,  $n_D^{18.5}$  1.45942,  $n_D^{18.5}$  1.46462,  $n_D^{20}$  1.4530; 1:4-dimethylcyclohexane, b. p. 119.5—120.5°,  $D_4^{15.7}$  0.7722,  $D_4^{20}$  0.769,  $n_D^{15.7}$  1.42407,  $n_D^{15.7}$  1.42597,  $n_D^{15.7}$  1.43174,  $n_D^{15.7}$  1.43624,  $n_D^{20}$  1.4240; 1:2-dimethylcyclohexan-4-ol, b. p. 188—188.5°,  $D_4^{12.5}$  0.9118,  $D_4^{20}$  0.906,  $n_D^{12.5}$  1.45826,  $n_D^{12.5}$  1.46042,  $n_D^{12.5}$  1.46645,  $n_D^{12.5}$  1.47121,  $n_D^{20}$  1.4570; 1:4-dimethylcyclohexan-4-one, mobile oil, b. p. 187°,  $D_4^{12.6}$  0.9121,  $D_4^{20}$  0.906,  $n_D^{12.6}$  1.44871,  $n_D^{12.6}$  1.45094,  $n_D^{12.6}$  1.45712,  $n_D^{12.6}$  1.46208,  $n_D^{20}$  1.4476 (a second specimen purified through the semicarbazone, needles, m. p. 189°, had  $D_4^{12.5}$  0.9116,  $D_4^{20}$  0.906,  $n_D^{12.5}$  1.44856,  $n_D^{12.5}$  1.45068,  $n_D^{12.5}$  1.45692,  $n_D^{12.5}$  1.46188,  $n_D^{20}$  1.4473); a mixture of 1:2-dimethyl- $\Delta^3$ - and - $\Delta^4$ -cyclohexenes, obtained by the action of anhydrous oxalic acid on 1:2-dimethylcyclohexan-4-ol, b. p. 123.5—124.5°,  $D_4^{20}$  0.8059,  $n_D^{20}$  1.44290,  $n_D^{20}$  1.44529,  $n_D^{20}$  1.45205,  $n_D^{20}$  1.45757; 5-chloro-1:3:5-trimethylcyclohexane, b. p. 53—53.5°/10 mm.,  $D_4^{13.7}$  0.9344 ( $D_4^{13.9}$  0.9342)

$D_4^{20}$  0.929,  $n_D^{13.9}$  1.45566,  $n_D^{13.9}$  1.45775,  $n_D^{13.9}$  1.46412,  $n_D^{13.9}$  1.46925,  $n_D^{20}$  1.4550; 1:3:5-trimethylcyclohexane, b. p. 137.5°,  $D_4^{13.1}$  0.7777,  $D_4^{20}$  0.772,  $n_D^{13.1}$  1.42971,  $n_D^{13.1}$  1.43175,  $n_D^{13.1}$  1.43764,  $n_D^{13.1}$  1.44235,  $n_D^{20}$  1.4286; 1:2:5-trimethylcyclohexan-4-ol, viscous oil, b. p. 195—197°/760 mm. (?), 79—79.6°/10 mm.,  $D_4^{19.2}$  0.8988,  $D_4^{20}$  0.898,  $n_D^{19.2}$  1.45639,  $n_D^{19.2}$  1.45851,  $n_D^{19.2}$  1.46459,  $n_D^{19.2}$  1.46938,  $n_D^{20}$  1.4582; 1:2:5-trimethylcyclohexan-4-one, mobile oil, b. p. 195—196°,  $D_4^{17.4}$  0.8989,  $D_4^{20}$  0.897,  $n_D^{17.4}$  1.44797,  $n_D^{17.4}$  1.45010,  $n_D^{17.4}$  1.45618,  $n_D^{17.4}$  1.46112,  $n_D^{20}$  1.4489 (a second preparation, purified through the semicarbazone, small needles, m. p. 175.5—176.5°, had b. p. 194—195°,  $D_4^{14.35}$  0.8998,  $D_4^{20}$  0.895,  $n_D^{14.35}$  1.44827,  $n_D^{14.35}$  1.45039,  $n_D^{14.35}$  1.45647,  $n_D^{14.35}$  1.46140,  $n_D^{20}$  1.4479); 1:2:5-trimethylcyclohexane, b. p. 44—45°/12 mm., 140—141°/760 mm. (?),  $D_4^{16.9}$  0.7799,  $D_4^{20}$  0.778,  $n_D^{16.9}$  1.42860,  $n_D^{16.9}$  1.43056,  $n_D^{16.9}$  1.43632,  $n_D^{16.9}$  1.44099,  $n_D^{20}$  1.4292; 1:2:5-trimethyl- $\Delta^4$ -cyclohexene, obtained by the action of phosphoric oxide on 1:2:5-trimethylcyclohexan-4-ol and possibly containing a small proportion of 1:2:5-trimethyl- $\Delta^3$ -cyclohexene, b. p. 144—146°,  $D_4^{16.15}$  0.8078,  $D_4^{20}$  0.805,  $n_D^{16.15}$  1.44742,  $n_D^{16.15}$  1.44990,  $n_D^{16.15}$  1.45683,  $n_D^{16.15}$  1.46264,  $n_D^{20}$  1.4482; 1:2:4:5-tetramethylcyclohexan-4-ol, b. p. 83.2—86.8°/13 mm., 195—196°/760 mm. (?),  $D_4^{16.5}$  0.8997,  $D_4^{20}$  0.897,  $n_D^{16.5}$  1.45782,  $n_D^{16.5}$  1.45999,  $n_D^{16.5}$  1.46608,  $n_D^{16.5}$  1.47094,  $n_D^{20}$  1.4584; 4-chloro-1:2:4:5-tetramethylcyclohexane, colourless oil, b. p. 69—71°/10 mm.,  $D_4^{13.95}$  0.9406,  $D_4^{20}$  0.936,  $n_D^{13.95}$  1.46288,  $n_D^{13.95}$  1.46515,  $n_D^{13.95}$  1.47150,  $n_D^{13.95}$  1.47655,  $n_D^{20}$  1.4624; 1:2:4:5-tetramethylcyclohexane, b. p. 160.5—161.5°,  $D_4^{13.1}$  0.7910,  $D_4^{20}$  0.785,  $n_D^{13.1}$  1.43517,  $n_D^{13.1}$  1.43718,  $n_D^{13.1}$  1.44307,  $n_D^{13.1}$  1.44772,  $n_D^{20}$  1.4341; 1:2:4:5-tetramethyl- $\Delta^4$ -cyclohexene, colourless oil, b. p. 165—167°,  $D_4^{16.5}$  0.8199,  $D_4^{20}$  0.817,  $n_D^{16.5}$  1.45617,  $n_D^{16.5}$  1.45880,  $n_D^{16.5}$  1.46597,  $n_D^{16.5}$  1.47192,  $n_D^{20}$  1.4572; 1:1:3-trimethylcyclohexane, b. p. 137—138°,  $D_4^{25}$  0.7868 ( $D_4^{25.3}$  0.7866),  $D_4^{20}$  0.790,  $n_D^{25.3}$  1.43177,  $n_D^{25.3}$  1.43385,  $n_D^{25.3}$  1.43998,  $n_D^{25.3}$  1.44453,  $n_D^{20}$  1.4362; 1:1:3-trimethyl- $\Delta^2$ -cyclohexen-4-one, b. p. 194—196°,  $D_4^{16.3}$  0.9332,  $D_4^{20}$  0.930,  $n_D^{16.3}$  1.47622,  $n_D^{16.3}$  1.47951,  $n_D^{16.3}$  1.48857,  $n_D^{16.3}$  1.49645,  $n_D^{20}$  1.4779; 1:1:3-trimethylcyclohexan-4-one, b. p. 190—191°,  $D_4^{16.45}$  0.9045,  $D_4^{20}$  0.902,  $n_D^{16.45}$  1.44907,  $n_D^{16.45}$  1.45130,  $n_D^{16.45}$  1.45732,  $n_D^{16.45}$  1.46240,  $n_D^{20}$  1.4497.

H. W.

**Action of Chlorine on 3:5-Dichloro-1:1-dimethyl- $\Delta^{2:4}$ -cyclohexadiene.** LEONARD ERIC HINKEL (T., 1920, 117, 1296—1303).

**Process for the Reduction of Aromatic Nitro-compounds.** JOSEPH TCHERNIAC and SAMUEL HENRY DAVIES (Brit. Pat. 150412).—Aromatic nitro-compounds, particularly hydroxynitro-compounds, are reduced by treatment with a mixture of hydriodic and hydrochloric acids. The consumption of iodine may be reduced to a minimum by adding a substance, such as phosphorus, which in presence of water reconverts the liberated iodine into hydriodic acid. In these circumstances it is obviously immaterial whether iodine or hydriodic acid is used in the first instance. For example, *p*-nitrophenol (139 parts) is reduced by boiling under a reflux condenser with 36 parts of amorphous phosphorus, 13.9 parts of

iodine, and 180 parts of 20% hydrochloric acid, until the vapour of iodine appears in the condenser. G. F. M.

**The Synthesis of some Nitro-derivatives of Toluene.**  
OSCAR LISLE BRADY and PERCY NOEL WILLIAMS (T., 1920, 117, 1137—1140).

**Binary Equilibria of certain Nitro-derivatives of Toluene.**  
M. GIUA (*Gazzetta*, 1920, 50, ii, 101—113).—Bell and Herty (this vol., i, 152) contradict the author's conclusion that molecular compounds are formed in the three binary systems, *p*-nitrotoluene-2:4:6-trinitrotoluene, *p*-nitrotoluene-2:4-dinitrotoluene, and 2:4-dinitrotoluene-2:4:6-trinitrotoluene (A., 1914, i, 817). The author refutes this contradiction, and gives further evidence in support of his conclusions. The experimental data obtained by Wogrinz and Vári (this vol., i, 307) also support the author's case. T. H. P.

**Solubility and Crystallisation of Trinitro-*m*-xylene in Different Solvents.** LOUIS DESVERGNES (*Ann. Chim. anal.*, 1920, [ii], 2, 278—284).—The following quantities of trinitro-*m*-xylene are dissolved per 100 c.c. of solvent:—Ethyl alcohol at 15°, 0.09 gram; at 78°, 0.65 gram. Amyl alcohol at 15°, 0.14 gram; at 128°, 10.3 grams. Acetone at 15°, 0.95 gram; at 57°, 4.27 grams. Ethyl acetate at 15°, 0.77 gram; at 76°, 5.43 grams. Glacial acetic acid at 15°, 0.4 gram; at 115°, 15.03 grams. Nitric acid (D 1.500) at 15°, 5.51 grams; at 90°, 51.1 grams. Benzene at 15°, 0.92 gram; at 80°, 10.0 grams. Chlorobenzene at 15°, 1.06 grams; at 180°, 108.53 grams. Nitrobenzene at 15°, 2.56 grams; at 90°, 19.60 grams. Carbon tetrachloride at 15°, 0.08 gram; at 75°, 0.96 gram. Toluene at 15°, 1.11 grams; at 110°, 21.7 grams. *m*-Xylene at 15°, 0.83 gram; at 90°, 9.25 grams. The crystals obtained from these solutions are in the form of needles, m. p. 180.5—182.5°. The solubility in aniline at 15° is 3.87 grams per 100 c.c.; boiling aniline reacts with trinitro-*m*-xylene, yielding substances which have not yet been investigated. W. P. S.

***p*-Toluenesulphonyl Derivatives of Amino-acids.**  
TAKESABURO OSEKI (*J. Tokyo Chem. Soc.*, 1920, 41, 8—19).—The following *p*-toluenesulphonyl derivatives have been prepared by shaking a solution of the amino-acid in the equivalent amount of alkali with an ethereal solution of *p*-toluenesulphonyl chloride for two hours, sodium hydroxide being frequently added to neutralise the hydrochloric acid formed in the reaction; the products are recrystallised after treatment with hydrochloric acid: of glycine, needles, m. p. 146°; of alanine, needles, m. p. 92—94°; of valine, m. p. 110—111°; of leucine, needles, m. p. 111.5°; of phenylalanine, needles, m. p. 134—135°; of cystine, octahedra, m. p. 204—205°; of asparagine, m. p. 126—128°; of tyrosine, columns, m. p. 224—226° (this derivative does not give the Millon reaction, and

is insoluble in alkalis; by treatment with excess of hydrochloric acid it is converted into the derivative

$\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{NH}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$ ,  
m. p. 117—119°; of tryptophan, needles, m. p. 176°; and of lysine and arginine, oils.

CHEMICAL ABSTRACTS.

**Mixed Crystals of 4 : 4'-Dichlorodiphenyl, 4 : 4'-Dibromodiphenyl, and 4 : 4'-Dimethyldiphenyl.** K. MIELEITNER (*Zeitsch. Kryst. Min.*, 1920, 55, 631—634).—Solutions in acetone of two of the compounds in variable proportions yielded measurable crystals with only a very limited range of miscibility in the case of the dichloro- and dibromo-compounds. The axial ratios (tabulated below) of the mixed crystals do not always lie between those of the corresponding pure compounds. An intimate interpenetration, rather than true isomorphous mixing, is therefore suggested.

Dichloro- Per cent.	Dibromo- Per cent.	Dimethyl- Per cent.	<i>a</i> -axis.	<i>c</i> -axis.	D.
100·00	—	—	1·1569	0·7078	1·439
—	100·00	—	1·1181	0·6963	1·897
—	—	100·00	1·1722	0·7137	1·102
53·06	46·94	—	1·1278	0·6979	1·654
55·89	44·11	—	1·1316	0·6993	1·695
44·66	—	55·34	1·1504	0·7016	1·228
10·45	—	89·55	1·1802	0·7388	1·127
61·46	—	38·54	1·1571	0·7068	1·278
—	59·75	40·25	1·1416	0·6884	1·422

L. J. S.

### Action of Amines on Trinitrophenylmethylnitroamine.

THOMAS CAMPBELL JAMES, JAMES IVOR MORGAN JONES, and ROBERT ILLTYD LEWIS (T., 1920, 117, 1273—1280).

**New Syntheses of Hordenine.** ERNST SPÄTH and PHILLIP SOBEL (*Monatsh.*, 1920, 41, 77—90. Compare Barger, T., 1909, 105, 2193; Rosenmund, A., 1910, i, 241; Léger, A., 1910, i, 336; Voswinkel, A., 1912, i, 443).—An ethereal solution of magnesium *p*-anisyl bromide is slowly added to dichlorodiethyl ether dissolved in ether at -15°, and the product, after being distilled under diminished pressure [b. p. 162—167°/16 mm. (decomp.)], is found to consist of a mixture of  $\beta$ -chloro- $\alpha$ -*p*-methoxystyrene,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CHCl}$ , colourless liquid with an odour of aniseed, b. p. 137—140°/19 mm., and the desired  $\beta$ -chloro- $\alpha$ -ethoxy- $\alpha$ -*p*-anisylethane,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OEt})\cdot\text{CH}_2\text{Cl}$ , the latter having partly lost ethyl alcohol during the process of distillation. The undistilled product of the reaction is, however, converted by anhydrous dimethylamine into  $\beta$ -dimethylamino- $\alpha$ -ethoxy- $\alpha$ -anisylethane,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OEt})\cdot\text{CH}_2\cdot\text{NMe}_2$ , b. p. 152—153°/14 mm. (the *platnichloride* was analysed), which could not be satisfactorily converted into hordenine, since short treatment with hydriodic acid yielded a base which was not identical with hordenine, whilst pro-

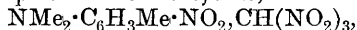
longed action caused the elimination of nitrogen with the formation of non-basic products.

*p*-Methoxybenzyl bromide reacts with bromomethyl ether in dry ethereal solution to give a mixture of 4:4'-dimethoxydibenzyl and  $\beta$ -methoxy- $\alpha$ -*p*-anisylethane,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OMe}$ , colourless liquid, b. p. 119—121°/12 mm. (the yield of the latter being 48% of that theoretically possible on the basis of the bromide used). Concentrated hydrobromic acid transforms the latter into  $\beta$ -bromo- $\alpha$ -*p*-hydroxyphenylethane, colourless, silky needles, m. p. 89—91°, b. p. 153—165°/14.5 mm. (some decomp.), which is converted by anhydrous dimethylamine at the ordinary temperature into hordenine, m. p. 117—118° in 82% yield.

$\beta$ -Bromo-*p*-methoxystyrene reacts extremely slowly with an alcoholic solution of sodium acetate at 170°, but is converted by methyl alcoholic sodium methoxide at 160—170° into a mixture of  $\beta$ -*p*-dimethoxystyrene,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{OMe}$ , b. p. 140—145°/16 mm., and *p*-anisylacetylene. The former is catalytically hydrogenated in the presence of palladised barium sulphate to  $\beta$ -methoxy- $\alpha$ -anisylethane, b. p. 121—123°/14 mm., which is converted into hordenine as described above, whilst the latter may be in part transformed into  $\beta$ -*p*-dimethoxystyrene by heating it with methyl alcoholic potassium hydroxide solution at 130—140°. H. W.

**Tetranitromethane. II. Tetranitromethane as a Nitrating Agent.** ERICH SCHMIDT and HEINRICH FISCHER (*Ber.*, 1920, 53, [B], 1529—1537).—Decomposition of tetranitromethane into nitroform and nitric acid which has been shown previously (A., 1919, i, 248) to occur almost exclusively under the action of very concentrated aqueous alkali is found to take place in the presence of a weak base if solutions in alcohol or acetone are employed. This is shown to occur at the instances of dimethyl- and diethyl-*p*-toluidine, which thereby undergo nitration by the liberated nitric acid. The same effect can be obtained with suitable non-basic materials if the reaction is performed in the presence of pyridine (which thereby forms the nitroform salt). The process thus constitutes the first method of introducing the nitro-group into the aromatic nucleus in a non-acid medium.

3-Nitrodimethyl-*p*-toluidine-nitroform,



yellow crystals which slowly decompose when preserved at the ordinary temperature, and evolve gas at 91—92°, is prepared by the gradual addition of an alcoholic solution of tetranitromethane to an ice-cold solution of dimethyl-*p*-toluidine and boric acid in alcohol. (The analysis of this and similar compounds is effected by estimating the nitroform, since they do not give concordant results for carbon, hydrogen, and nitrogen by the usual method.) The constitution of the substance is elucidated by its reduction to 3-aminodimethyl-*p*-toluidine, b. p. 115—117°/12 mm., 69—71°/0.5 mm. (acetyl derivative, m. p. 111—112°), by its fusion by alkali into 3-nitrodimethyl-*p*-toluidine, b. p. 110—113°/0.5 mm., and

by its direct synthesis from its components in aqueous-alcoholic solution. 3-Nitrodiethyl-*p*-toluidine-nitroform, yellow crystals which decompose at 91°, is similarly converted into 3-nitrodiethyl-*p*-toluidine, b. p. 101—102°/0·2 mm. 3-Nitrodimethyl-*p*-anisidine-nitroform, yellow crystals which decompose at 108° after previous discoloration and can only be preserved for a few hours at the ordinary temperature, and 3-nitrodimethyl-*p*-anisidine, b. p. 108—110°/0·5 mm., are prepared in like manner.

The action of an alcoholic solution of tetranitromethane on *p*-cresol dissolved in an ice-cold mixture of alcohol and pyridine yields *m*-nitro-*p*-cresol, m. p. 33·5°, b. p. 73—75°/0·5 mm., in 60% yield, and pyridine nitroform, which decomposes at 91—92° and cannot be long preserved unchanged at the ordinary temperature.

[With ADALBERT WAGNER.]—A solution of isosafrole in acetone and pyridine is converted by tetranitromethane dissolved in acetone into  $\beta$ -nitroisosafrole, m. p. 98° (compare Wallach and Müller, A., 1904, i, 754), the yield being 72·5% of that theoretically possible.

[With WILLY BÄJEN.]—Anethole is similarly transformed into  $\beta$ -nitroanethole, m. p. 48°, in 64·3% yield. H. W.

### Tetranitromethane. III. Conversion of Tertiary Amines into Secondary Nitrosoamines. I. ERICH SCHMIDT and HEINRICH FISCHER (Ber., 1920, 53, [B], 1537—1544).

—When tetranitromethane is allowed to act on a boiling alcoholic solution of a tertiary base in the presence of pyridine, the nitrating action of the liberated nitric acid (compare preceding abstract) is only slightly evident, the main change consisting in the removal of an N-alkyl group as the corresponding aldehyde and the formation of a second-

ary nitrosoamine:  $\text{:N}\cdot\text{CH}_2\text{R} + \text{C}_5\text{H}_5\text{N} + (\text{NO}_2)_2\text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{---} \end{array} \text{N}\cdot\text{O}\cdot\text{NO}_2 = \text{:N}\cdot\text{NO} + \text{C}_5\text{H}_5\text{N}\cdot\text{CH}(\text{NO}_2)_3 + \text{R}\cdot\text{CHO}$ . The action has so far been applied to fatty-aromatic amines, and does not appear to be influenced by the presence or position of further substituents in the ring. It is usually carried out in the following manner. An alcoholic solution of tetranitromethane (1·1 mol.) is slowly added to a boiling alcoholic solution of the tertiary amine (1 mol.) and pyridine (1·2—1·5 mol.), and ebullition is continued until the odour of tetranitromethane disappears. The mixture is poured into water and extracted with ether after addition of saturated salt solution. The ethereal solution is subjected to the action of steam in the presence of a further quantity of salt solution and a little potassium carbonate. Ether and the nitrosoamine are successively volatilised; the latter is freed from traces of pyridine by agitating its ethereal solution with dilute sulphuric acid, and subsequently purified in the usual manner. The following substances have been thus obtained: phenylmethylnitrosoamine, b. p. 86—87°/1·7 mm., and *p*-nitrophenylmethylnitrosoamine; phenylethylnitrosoamine, b. p. 96—97°/1·9 mm., and *p*-nitrophenylethylnitrosoamine; *o*-tolylmethylnitrosoamine, b. p. 89—90°/1·5 mm.; *o*-tolylethylnitrosoamine, b. p. 83—84°/0·6 mm.; *o*-chlorophenylmethylnitrosoamine, b. p. 89°/



1.2 mm.; *o*-anisylmethylnitrosoamine, b. p. 112°/1.1 mm., and *p*-nitro-*o*-anisylmethylnitrosoamine; *m*-tolylmethylnitrosoamine, orange-yellow oil, b. p. 89—90°/1 mm.; *m*-chlorophenylmethylnitrosoamine, nearly colourless leaflets, m. p. 36—37°; *p*-tolylmethylnitrosoamine, m. p. 52°, and 3-nitrodimethyl-*p*-toluidine; *p*-chlorophenylmethylnitrosoamine, m. p. 51°; *p*-chlorophenylethylnitrosoamine, colourless, interwoven needles, m. p. 60—61° (*p*-chlorodiethylaniline, which has been previously isolated by Hofmann in the crude condition, is obtained by the action of ethyl alcohol on *p*-chloroaniline hydrobromide at 150°, and forms colourless needles, m. p. 30°, b. p. 95—96°/1.5 mm.); *m*:4-xylylmethylnitrosoamine, pale yellow oil, b. p. 101°/1.3 mm. H. W.

**Halogenalkylated Aromatic Amines. V. Preparation of Aryl Vinyl Ethers.** JULIUS VON BRAUN and GEORG KIRSCHBAUM (*Ber.*, 1920, **53**, [B], 1399—1408).—The preparation of vinyl ethers is generally a matter of considerable difficulty, and few members of this class are known. The authors have therefore investigated a possible general method of synthesis which depends on (1) the replacement of the halogen atom of  $\beta$ -halogenalkylated aromatic amines by the radicle OR; (2) union of the basic ethers thus produced with methyl iodide or methyl sulphate; and (3) decomposition of the quaternary salts so formed with alkali in accordance with the scheme  $\text{RO} \cdot [\text{CH}_2]_2 \cdot \text{NR}_3' \cdot \text{I} + \text{KOH} \rightarrow \text{R} \cdot \text{O} \cdot \text{CH} : \text{CH}_2 + \text{NR}_3$ . Unfortunately, the process breaks down at the third stage, when R is an aliphatic residue, since the quaternary compounds are only decomposed with unusual difficulty, and are, in part, extensively changed and in part re-converted into the basic ether. With phenols, on the other hand, good results are obtained, and this is also the case with dihydroxy- and thio-phenols.

Peculiar interest attaches to the vinyl ethers from the point of view of the chemistry of perfumes, but the introduction of the vinyl complex is found to have a most irregular influence on the odour of the compounds produced.

N- $\beta$ -Naphthoxyethylmethylaniline,  $\text{C}_{10}\text{H}_7 \cdot \text{O} \cdot [\text{CH}_2]_2 \cdot \text{NMePh}$ , m. p. 75°, b. p. 200—205°/mercury vacuum, is most readily prepared by heating  $\beta$ -naphthol with methylbromoethylaniline and potassium hydroxide in acetone solution. It is only feebly basic, but yields a *hydrochloride*, needles, m. p. 150°, a *platinichloride* decomposing at 128—129°, and a *methiodide*, m. p. 137°. Decomposition of the latter is best effected with boiling aqueous potassium hydroxide (15%), through which steam is blown continuously, whereby dimethylaniline and  $\beta$ -naphthyl vinyl ether are removed as soon as they are formed, whilst N- $\beta$ -naphthoxyethylmethylaniline remains in the flask. The yield of the ether is 45—50% of that theoretically possible, whilst about a half of the original iodide is left as the corresponding base, which can be readily utilised for further preparations.  $\beta$ -Naphthyl vinyl ether, m. p. 63—64°, b. p. 137°/13 mm., has an intense odour of tangerine skins. In contrast to allyl ether (the same is true for all other representatives of this

class), it is not able to undergo the Claisen transformation into vinylated  $\beta$ -naphthol; the vinyl group does not unite with bromine smoothly, and is only very slowly and incompletely hydrogenated by Paal's method. The aromatic vinyl ethers are more stable towards hydrolysis than are the corresponding aliphatic compounds, and the odour of acetaldehyde is only apparent after protracted boiling with alkali hydroxide or dilute acid.

*Carvacryloxyethylmethylaniline*,  $C_6H_3MePr \cdot O \cdot [CH_2]_2 \cdot NMePh$ , is a moderately viscous oil, b. p. 220—221°/11 mm., which yields a very soluble *picrate*, and an oily *hydrochloride* and *methiodide* (the *platinichloride* corresponding with the latter has m. p. 90°). *Carvacryl vinyl ether* has b. p. 217—218°/atmospheric pressure, and possesses an unpleasant odour dissimilar to that of the corresponding methyl or ethyl ether.

$\beta$ -*Tetrahydronaphthylloxyethylmethylaniline*, b. p. 52—53°, b. p. 257—258°/14 mm., gives a *hydrochloride*, m. p. 163°, a *picrate*, m. p. 122°, and a *methiodide*, colourless, crystalline powder, m. p. 123°.  $\beta$ -*Tetrahydronaphthyl vinyl ether*, b. p. 121—122°/11 mm., has a faint, not unpleasant odour, which is less marked than that of the corresponding *allyl ether*, b. p. 158—161°/23 mm.

The action of methylbromoethylaniline on catechol leads to a mixture of *o*-hydroxyphenoxyethylmethylaniline, m. p. 71° (the *hydrochloride*, m. p. 195° after darkening above 140°, *picrate*, orange leaflets, m. p. 146°, *acetyl* derivative and *methiodide*, colourless leaflets, m. p. 135°, are described), and the symmetrical *bis*- $\beta$ -methylphenylaminoethyl ether of catechol,

$NMePh \cdot [CH_2]_2 \cdot O \cdot C_6H_4 \cdot O \cdot [CH_2]_2 \cdot NMePh$ , m. p. 90—91° (*hydrochloride*, *picrate*, yellow powder, m. p. 103°, *methiodide*, m. p. 96°). *Catechyl monovinyl ether*, b. p. 213°, is a colourless liquid with a faint odour. *Catechyl divinyl ether* has b. p. 206—209°.

*Phenylthioethylmethylaniline*,  $SPh \cdot [CH_2]_2 \cdot NMePh$ , almost odourless oil, b. p. 222—224°/14 mm. (*hydrochloride*, oily, *picrate*, yellow needles, m. p. 155°), yields an oily *methiodide* (the corresponding *platinichloride*, m. p. 155°, was analysed), which gives a 90% yield of *phenyl vinyl sulphide*, b. p. 200—201°, almost colourless liquid, which has a pleasant odour of radishes.

*N-Methyl- $\beta$ -amyloxyethylaniline*, b. p. 154—156°/10 mm., is slowly formed in the usual manner; it yields oily salts and a non-crystalline *methiodide* (the corresponding *platinichloride* decomposes at 166° after darkening at 160°); when treated with potassium hydroxide, the quaternary iodide largely regenerates the original amine and only gives traces of a nitrogen-free oil with an ethereal odour.

*N-Methyl- $\beta$ -thiocyanoethylaniline*, pale yellow oil, b. p. 186°/10 mm., is obtained with unusual ease from methyl- $\beta$ -bromoethylaniline and potassium thiocyanate in aqueous-alcoholic solution, and yields a crystalline *methiodide*, m. p. 137—138°. The latter appears to be decomposed by potassium hydroxide primarily into dimethylaniline and *vinyl thiocyanate*; under the experimental conditions

adopted, however, the latter is unstable, and immediately decomposes in an undetermined direction.

H. W.

**Studies in Ring Formation. III. The Condensation of Aromatic Amines with  $\alpha$ - and  $\beta$ -Diketones and with 4:4'-Diacetyldiphenyl.** CLARENCE VICTOR FERRISS and EUSTACE EBENEZER TURNER (T., 1920, 117, 1140—1151).

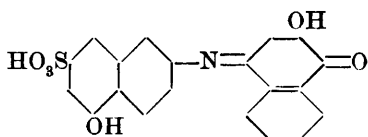
**Influence of Substituents on Reactions. IV. Preferential Substitution Positions in  $\beta$ -Naphthylamine.** HARTWIG FRANZEN and GUSTAV STÄUBLE (*J. pr. Chem.*, 1920, [ii], 101, 58—74. Compare A., 1919, ii, 4).—It has been shown previously (Franzen and Aaslund, A., 1917, i, 644) that not more than three bromine atoms can be introduced readily into the  $\beta$ -naphthylamine molecule, forming successively 1-bromo- $\beta$ -naphthylamine, 1:6-dibromo- $\beta$ -naphthylamine (compare Claus and Philipson, A., 1891, 462), and a substance which has been considered by Claus and Jäck to be 1:4:6-tribromo- $\beta$ -naphthylamine, but which is now shown to be the 1:3:6-derivative; this is deduced from the fact that the compound is converted by tin and hydrochloric acid into a dibromo- $\beta$ -naphthylamine, which differs from the 1:6-derivative and after elimination of the amino-group yields 2:7-dibromonaphthalene. The authors are led to the conclusion that the positions 1, 6, and 3 are preferential substitution points in the bromination of  $\beta$ -naphthylamine; the  $\beta$ -amino-group has a much greater influence on the 1- than on the 6-hydrogen atom, whilst the latter is noticeably more influenced than the 3-hydrogen atom. The action of tin and hydrochloric acid on 1:6-dibromo- $\beta$ -naphthylamine and 1:3:6-tribromo- $\beta$ -naphthylamine leads essentially to the replacement of the 1-bromo-atom by hydrogen; in these two substances, the position 1 is a favoured substitution point with respect to hydrogen. In these cases also, therefore, the substituent in position 1 is much more influenced by the amino-group than that in position 3 or 6.

$\alpha$ -Bromonaphthalene is not reduced by tin and hydrochloric acid. 1-Bromo- $\beta$ -naphthylamine is converted by tin and hydrochloric acid or by stannous chloride into  $\beta$ -naphthylamine, but is not affected by alcoholic potassium hydroxide solution. 1:6-Dibromo- $\beta$ -naphthylamine is transformed by tin and hydrochloric acid, by stannous chloride, by hydriodic acid or by cuprous chloride and hydrochloric acid into 6-bromo- $\beta$ -naphthylamine, m. p. 128° (the hydrochloride, *acetyl* derivative, m. p. 192°, and *benzoyl* derivative, colourless leaflets, m. p. 218°, are described). 6-Bromo- $\beta$ -naphthylamine is scarcely affected by tin and hydrochloric acid or by hydriodic acid. 1:3:6-Tribromo- $\beta$ -naphthylamine is reduced by tin and hydrochloric acid to 3:6-dibromo- $\beta$ -naphthylamine, small, colourless leaflets, m. p. 187° (*acetyl* derivative, long, slender needles, m. p. 195°, *benzoyl* derivative, long, silky needles, m. p. 161—162°); a similar result is obtained by the use of stannous chloride. H. W.

**The Preparation of Thiocarbimides from Non-Aromatic Primary Bases.** JULIUS VON BRAUN (*Ber.*, 1920, 53, [B], 1588).—Thiocarbimides of non-aromatic primary bases are most conveniently prepared by the thiuram disulphide method (van Braun and Deutsch, A., 1912, i, 673), which is particularly applicable to the production of fatty-aromatic, hydroaromatic, and complex thiocarbimides. *cyclo*Hexylthiocarbimide (compare Skita and Rolfs, this vol., i, 607) is obtained quantitatively from *cyclo*hexylamine in this manner. H. W.

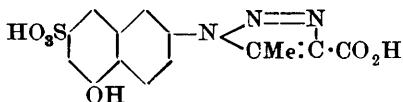
**New Derivatives of J-acid [6-Amino-1-naphthol-3-sulphonic Acid].** W. KÖNIG and H. HALLER (*J. pr. Chem.*, 1920, [ii], 101, 38—57).—The experiments were undertaken with the object of elucidating the causes which condition the peculiar tinctorial properties of derivatives of J-acid as compared with those derived from similar acids. In most of the work which has been accomplished previously, the alterations have been effected by alkylating, arylating, etc., the amino-group. The present communication describes the production of compounds obtained by replacement of the amino- by other radicles and by altering the sulphonic acid group; the consideration of the tinctorial properties of the substances is reserved for a subsequent paper. The following individual substances are described, which are generally prepared by well-known methods. In the case of the sulphonic acids, the *p*-toluidine salts have been investigated, since the free acids and the simple alkali salts are inconveniently freely soluble in water.

*p*-Toluidine 6-iodo-1-naphthol-3-sulphonate, pale pink leaflets;  
*p*-toluidine 6-chloro-1-naphthol-3-sulphonate, grey leaflets;



*p*-toluidine 6-azido-1-naphthol-3-sulphonate, shining, transparent, colourless leaflets (the disodium salt is also described);  
 6-β-hydroxynaphthaquinonimido-1-naphthol-3-sulphonic acid (annexed formula), violet

powder; 6-hydrazino-1-naphthol-3-sulphonic acid, small, colourless needles; *p*-toluidine 6-isatin-1-hydroxy-2-naphthylhydrazine-3-sulphonate, lemon-yellow powder; 1(7'-sulpho-5'-hydroxy-2'-naphthyl)-5-methyl-1 : 2 : 3-triazole-4-carboxylic acid (annexed



formula), colourless needles by the action of ethyl acetoacetate on *p*-toluidine 6-azido-1-naphthol-3-sulphonate in the presence of alcoholic sodium ethoxide, followed by hydrolysis

of the product with sodium hydroxide; sodium 5:5'-dibenzoyloxy-2:2':1:1'-dinaphthacarbazole-7:7'-disulphonate; sodium 6-benzoylamino-1-benzoxynaphthalene-3-sulphonate, small, silky needles; 6-benzoylamino-1-benzoyloxynaphthalene-3-sulphonyl chloride, yel.

low glassy mass, m. p.  $151^{\circ}$ ; the corresponding *anilide*, colourless crystals, m. p.  $155^{\circ}$ ; 6-benzoylamino- $\alpha$ -naphthol-3-sulphonanilide (from the dibenzoyl compound and dilute sodium hydroxide solution), pale yellow powder, m. p.  $125^{\circ}$ , which readily couples with diazotised *p*-toluidine to yield a pale red, monoazo-dye; phenyl-2-benzoylamino-5-hydroxy-7-naphthylsulphone (from the corresponding acid chloride, benzene, and aluminium chloride), pale yellow powder, which blackens without melting when heated.

In connexion with the conversion of *J*-acid by bisulphite into "carbazole *J*-acid," the mechanism of Bucherer's reaction is fully discussed; the author is led to the conclusion that the primary products are sulphurous esters, but the original paper must be consulted for details.

H. W.

**Alkali Fusions. II. Fusion of Sodium Benzene-*m*-disulphonate with Sodium Hydroxide for the Production of Resorcinol.** MAX PHILLIPS and H. D. GIBBS (*J. Ind. Eng. Chem.*, 1920, **12**, 857—860).—The maximum yield of resorcinol is obtained by fusing 20 to 24 mols. of sodium hydroxide with 1 mol. of sodium benzene-*m*-disulphonate, but in practice the yields were nearly as good (60.1 to 63.5%) when only 16 mols. of alkali were used. The best temperature was  $310^{\circ}$ , and the time two hours. At  $330$ — $350^{\circ}$  there was some destruction of resorcinol, whilst at  $270$ — $290^{\circ}$  the yields were lower, owing to the reaction being incomplete, and even by extending the time of fusion were not so good as at  $310^{\circ}$ . The presence of water in the fusion mixture reduces the yield of resorcinol, but does not make a very material difference if it does not exceed 2 to 4%.

C. A. M.

**Tautomerism of Phenols. Resorcinol.** HANS TH. BUCHERER (*Ber.*, 1920, **53**, [B], 1457—1459).—The action of sodium hydrogen sulphite on a boiling aqueous solution of resorcinol slowly leads to the formation of a substance,  $C_6H_9O_{11}S_3Na_3$ , which has been regarded by Fuchs and Elsner (this vol., i, 545) as the sodium salt of the bisulphite compound of cyclohexane 3:5-dionesulphonic acid. The stability of this compound towards boiling dilute mineral acids causes the author to doubt the constitution assigned to it and to consider it as allied to the sulphurous esters of mono- and di-hydric phenols, which he has shown to be characterised in this manner. It is further pointed out that Bucherer and Schenkel (*A.*, 1908, i, 452) have obtained a compound,  $C_5H_5N, 3NaHSO_3, 2H_2O$ , from pyridine and bisulphite in which the pyridine nucleus is extensively altered, since the greater part of the pyridine nitrogen is readily liberated in the form of ammonia by cold dilute alkali; it therefore appears that cyclic systems with two or three molecules of bisulphite can be obtained readily and without the necessity of intervention of carbonyl groups.

H. W.

**Tautomerism of Resorcinol.** J. HERZIG and S. ZEISEL (*Ber.*, 1920, **53**, [B], 1518).—In connexion with the recent publication

on this subject by Fuchs and Elsner (this vol., i, 545), the authors point out that they have conclusively proved the possibility of tautomerism in this substance by the action of potassium hydroxide and alkyl iodide.

H. W.

**Syntheses of Humic Acids.** WILHELM ELLER and KÄTE KOCH (*Ber.*, 1920, 53, [B], 1469—1476).—The oxidation of phenols in alkaline solution leads to the formation of substances which appear to be identical in all respects with the natural humic acids; only such phenols, however, as are capable of giving quinonoid intermediate products show this behaviour. The acids are obtained by allowing the alkaline solutions of the phenol to remain exposed to the air, or, more rapidly, by the addition of finely powdered potassium persulphate to the solution. The products from catechol, quinol, and *p*-benzoquinone give analytical figures in agreement with the formula  $C_6H_4O_3$ , but since the acids do not crystallise and cannot be purified by repeated precipitation, the purity of the substances can only be controlled by analysis of several independently prepared specimens. The synthetic substances are soluble in water and alcohol, and, to some extent, in ether, but this property is lost when they become dry. In proportion as they are washed free from mineral acid, they develop the power of forming colloidal solutions in water. The moist substances shrink greatly when dried, and at  $100^\circ$  lose water, forming hard, brittle masses, which are readily ground to a black, shining powder. Their alkali salts dissolve readily, the remaining salts very sparingly, in water. In these respects they behave exactly as do the natural humic acids, and the similarity also extends to their behaviour towards chlorine, nitric acid, sodium hypobromite, and acetic anhydride.

The humic acid obtained from phenol resembles the other synthetic products, except in its greater solubility in alcohol; it has, however, been so far impossible to obtain concordant analytical data for the product.

The work is considered to throw considerable light on the chemistry of the natural humic acids, since it proves definitely that a number of them are existant, and that the pure substances are free from nitrogen and are possessed of definite acidic properties (probably owing to the presence of an unchanged phenolic hydroxyl group). They are probably formed by elimination of water from the hexoses, with formation of quinones,  $C_6H_{12}O_6 = 4H_2O + C_6H_4O_2$ , and subsequent oxidation of the latter to humins; an experimental realisation of the first step in this hypothetical scheme has not yet been accomplished satisfactorily.

H. W.

**Diphenylene Sulphide in Coal Tar.** O. KRUBER (*Ber.*, 1920, 53, [B], 1566—1567. Compare Weissgerber and Kruber, this vol., i, 754).—The presence of diphenylene sulphide in crude phenanthrene (containing about 1% of sulphur) is established by

oxidising the latter with hydrogen peroxide in acetic acid solution, whereby diphenylenesulphone, m. p. 229—230°, is obtained.

H. W.

**Diphenylaryltelluronium Salts.** KARL LEDERER (*Ber.*, 1920, 53, [B], 1430—1445. Compare A., 1916, i, 810; 1917, i, 134).—The preparation of the diphenylaryltelluronium salts is effected by the addition of the requisite Grignard reagent (two or, more usually, three times the calculated quantity is used) to a solution of diphenyltelluronium dichloride in dry toluene. The mixture is shaken and immediately treated with dilute hydrochloric acid, after which any residual solid is dissolved in boiling water. The solution is treated with potassium iodide in quantity sufficient to convert the telluronium salt into the iodide, when the latter separates, whilst a further quantity may be obtained by treatment of the filtrates with sulphurous acid, and subsequent concentration. It is frequently contaminated with basic iodide, in which case it is again dissolved in water, the solution is treated with acetic acid and potassium iodide, and subjected to protracted boiling, whereby the basic iodide is decomposed, with the separation of the di-iodide, which can readily be separated by filtration. The following series are described.

*Diphenyl-p-tolyltelluronium Salts.*—*Iodide*, colourless, crystalline powder, m. p. 219—220°; *bromide*, colourless needles, m. p. 228—229° after softening at 226°; *chloride*, partly crystalline mass; *picrate*, monoclinic prisms, m. p. 132—133° after softening at 130°; *mercuri-iodide*, microscopic needles, m. p. 222—223° after softening at 220°; *mercurichloride*, resinous mass.

*Diphenyl-o-tolyltelluronium Salts.*—*Iodide*, small crystals, m. p. 175—176° after softening at about 170° (*mercuri-iodide*, white, amorphous powder, which softens from about 154° and is completely melted at 184°); *chloride*, a resin; *mercurichloride*, colourless needles, m. p. 210—211° after softening at 207—208°; *bromide*, microscopic prisms, m. p. about 203° after softening at about 199°; *picrate*, small, triclinic crystals, m. p. 127—128° after softening at 122°.

*Diphenyl-m-tolyltelluronium Salts.*—*Iodide*, colourless needles, m. p. 190—191° (from water), 202° after softening at 200° (from alcohol); *mercuri-iodide*, cubic crystals from alcohol, m. p. 134—135° after softening at 132°, slender needles from glacial acetic acid, m. p. 132—133° after softening at 129°; the *chloride* and *mercurichloride* are resinous; *bromide*, needles, m. p. 202—203° after softening at 199° (*mercuribromide*, semi-solid mass); *picrate*, m. p. 105—106° after softening at 101°.

*Triphenyltelluronium Salts.*—*Iodide*, m. p. 247—248° after softening from 245°; *mercuri-iodide*, small, colourless plates, which darken at 146°, soften at 155°, and are molten at about 178°; *mercuribromide*, long, colourless needles, m. p. 143—144° (decomp.); *mercurichloride*, four-sided rods, m. p. 136—137° after softening at 130° (from water), slender, silky needles, m. p. 138—139° after softening at 135° (from glacial acetic acid).

*Diphenyl-o-xylyltelluronium iodide*, microscopic cubes (+2EtOH), m. p. 114—115° with effervescence. *Diphenyl-m-xylyltelluronium iodide*, colourless powder, m. p. about 103° after softening at 92°; *mercuri-iodide*, colourless powder, m. p. 201—202° after softening at 195°.

*Diphenyl-p-xylyltelluronium Salts*.—*Iodide*, m. p. 213—214° after softening at 211°; *mercuri-iodide*, yellow, amorphous powder, m. p. about 110° after softening at 100°; *chloride*, m. p. 210—211° after softening at 207°; *mercurichloride*, m. p. about 176° after softening at 172°; *bromide*, small crystals, m. p. 207—208° after softening at 204° (from water), rods, m. p. 220—221° after softening at 218° (from alcohol-ether); *mercuribromide*, needles, m. p. 178—180° after softening at 174° (from alcohol), 174—175° after softening at 166° (from glacial acetic acid); *picrate*, small, yellow, rhombic crystals, m. p. 170—171° after softening at 168°.

*Diphenyl-p-anisyltelluronium Salts*.—*Iodide*, small prisms (+0.5EtOH); *mercuri-iodide*, white, amorphous powder, m. p. 89—90° after softening at 86°; the *chloride*, *bromide*, and their *mercuric* double salts are oily or resinous; *picrate*, small, yellow, monoclinic crystals, m. p. 126—127° after softening at 125°.

*Diphenyl-o-anisyltelluronium Salts*.—*Iodide*, colourless crystals, m. p. 230—231° after softening at 226°; *mercuri-iodide*, colourless leaflets, m. p. 218—219° after softening at 215°; the *chloride* and *mercurichloride* are resinous; *bromide*, m. p. 220—221° after softening at 215°; *picrate*, m. p. 165—166° after softening at 160—161°.

*Diphenyl-m-anisyltelluronium iodide* was obtained as a white, crystalline powder, which softened at 85° and was completely melted at about 95°; it was not isolated in the pure condition.

*Diphenyl-p-phenethyltelluronium Salts*.—*Iodide*, crystalline powder, m. p. about 131° after softening at 125°; *mercuri-iodide*, white, amorphous powder, m. p. 76—77° after softening at 74°.

*Diphenyl-o-phenethyltelluronium Salts*.—*Iodide*, m. p. 247—248° (decomp.) after softening at 225°; *mercuri-iodide*, colourless crystals, which become yellow in sunlight, m. p. about 183—184° after softening at 174°; the *chloride*, *mercurichloride*, and *picrate* form wax-like masses; *bromide*, colourless, crystalline powder, m. p. 178—179° after softening at 174°.

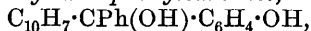
*Diphenyl-α-naphthyltelluronium Salts*.—*Iodide*, m. p. about 148° after softening at 130°; *mercuri-iodide*, m. p. 126° after softening at 115°; the *chloride* and *bromide* could only be isolated in an impure state.

*Diphenylmesityltelluronium iodide* has m. p. 153—154° after softening at 152°, whilst the *mercuri-iodide* is a white powder, m. p. 93—94° after softening at about 89°. H. W.

**Tautomerism in the Triarylcarbinols: Mono-*p*-hydroxydiphenyl-α-naphthylcarbinol.** M. GOMBERG and N. A. LANGE (*J. Amer. Chem. Soc.*, 1920, **42**, 1879—1883. Compare following abstract).—*Phenyl-α-naphthyl*dichloromethane,  $C_{10}H_7\cdot CPhCl_2$ , m. p.

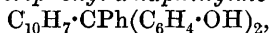


92°, obtained by the action of phosphorus pentachloride on phenyl  $\alpha$ -naphthyl ketone, when slowly added in benzene solution to a boiling solution of phenol in benzene gives *phenyl- $\alpha$ -naphthyl*diphenoxymethane,  $C_{10}H_7 \cdot CPh(OPh)_2$ , m. p. 169—170°. If, however, phenol and phenyl- $\alpha$ -naphthylchloromethane react together at the ordinary temperature for twelve hours and then at 50° for one hour the product is the fuchsone *phenyl- $\alpha$ -naphthyl*quinomethane,  $C_{10}H_7 \cdot CPh \cdot C_6H_4 \cdot O$ , m. p. 169—170°. If this fuchsone is boiled in alcoholic solution with aqueous sodium hydroxide until the colour of the solution has changed to a light yellow, and the solution is then diluted with water and saturated with ammonium chloride, *phenyl-p-hydroxyphenyl- $\alpha$ -naphthylcarbinol*,



is obtained in its quinonoid form, and it is not possible to isolate the benzenoid form. Thus, as in the case of its isomeride, diphenyl-4-hydroxy- $\alpha$ -naphthylcarbinol (*loc. cit.*), the naphthyl group exerts its tautomerising influence with the production of the quinonoid tautomeride.

When phenyl- $\alpha$ -naphthylchloromethane and phenol previously saturated with dry hydrogen chloride are heated at 110° for twenty-four hours and the product, after the removal of the excess of phenol by steam distillation, is poured into 5% aqueous sodium hydroxide, 4:4'-*dihydroxytriphenyl- $\alpha$ -naphthylmethane*,



m. p. 209—210° (decomp.), is obtained.

W. G.

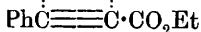
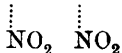
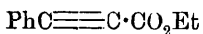
**Tautomerism in the Triarylcarbinol Series; Diphenyl-4-hydroxy-1-naphthylcarbinol and Diphenyl-2-hydroxy-1-naphthylcarbinol.** M. GOMBERG and F. W. SULLIVAN, jun. (*J. Amer. Chem. Soc.*, 1920, **42**, 1864—1870).—A quantitative yield of *p*-naphthafuchsone may be obtained by mixing together benzophenone chloride and  $\alpha$ -naphthol in a dry atmosphere, and after leaving the mixture overnight making it slightly alkaline with dilute sodium hydroxide and distilling it with steam. On bromination in acetic acid solution the fuchsone gives 3-bromo-*p*-naphthafuchsone, m. p. 176°, and on chlorination 3-chloro-*p*-naphthafuchsone, m. p. 161°. *o*-Naphthafuchsone was similarly obtained from benzophenone chloride and  $\beta$ -naphthol, but in this case the addition of aluminium chloride as a catalyst was necessary. When dissolved in alcoholic sodium hydroxide and an aqueous solution of ammonium chloride added to this solution, *p*-naphthafuchsone gave almost entirely the quinonoid form of *diphenyl-4-hydroxy- $\alpha$ -naphthylcarbinol*, whilst *o*-naphthafuchsone gave exclusively the benzenoid form of *diphenyl-2-hydroxy-1-naphthylcarbinol*. The bromo- and chloro-derivatives described above gave the quinonoid forms of *diphenyl-3-bromo-4-hydroxy-1-naphthylcarbinol* and *diphenyl-3-chloro-4-hydroxy-1-naphthylcarbinol* respectively.

Both *o*- and *p*-naphthafuchsones give additive compounds with hydrogen chloride, but the chloro- and bromo-naphthafuchsones do not.

W. G.

**Addition of Nitrogen Peroxide to Ethyl Phenylpropiolate.**

HEINRICH WIELAND [with HANS WAGNER] (*Ber.*, 1920, **53**, [B], 1343—1346).—When nitrogen peroxide is passed into a cold solution of ethyl phenylpropiolate in light petroleum, colourless, prismatic crystals readily separate, which rapidly decompose into the original materials when filtered. Analysis of the compound is effected by the addition of an unweighed portion of the material to *N*/10-potassium hydroxide solution in the presence of ether and subsequent estimation of the ethyl phenylpropiolate and the amount of alkali used and of potassium nitrite formed. It is thus shown that one molecule of nitrogen peroxide is absorbed for each molecule of ester, and it is suggested that the molecules are united by means of the partial valencies of the acetylenic carbon atoms, as indicated by the annexed formula.



[With E. SCHAMBERG.]—When the primary labile additive compound is allowed to remain overnight in contact with light petroleum, it decomposes into ethyl phenylpropiolate and a mixture of the stereoisomeric ethyl  $\alpha\beta$ -dinitrocinnamates, of which the *modification*, almost colourless needles, m. p. 66.5°, has been isolated.

H. W.

**Preparation of Tropic Acid from Ethyl Formylphenylacetate.** JULIUS VON BRAUN (*Ber.*, 1920, **53**, [B], 1409).—Recently McKenzie and Wood (*T.*, 1919, **115**, 228) have found that tropic acid can only be obtained in 16—30% yield by the reduction of ethyl formylphenylacetate with aluminium amalgam, and subsequent hydrolysis of the tropic ester. This result does not agree with the author's experience, since he finds the yield of acid to be about 50% of that theoretically possible, whilst a half of the original ester remains combined with the aluminium hydroxide, from which it can be recovered by acidification and extraction with ether. The difference is possibly to be ascribed to the use of insufficiently active aluminium amalgam.

H. W.

**Esterification of Unsymmetrical Di- and Poly-basic Acids.****XXIX. Esterification of 4-Dimethylaminoisophthalic Acid.**

NIKOLA SMOPLAKA (*Monatsh.*, 1920, **41**, 115—124. Compare Wegscheider, Malle, Ehrlich, and Skutezky, A., 1919, i, 76).—1-Methyl 3-hydrogen 4-dimethylaminoisophthalate, colourless prisms or crystalline powder, m. p. 180°, is formed by the esterification of the acid with methyl-alcoholic hydrogen chloride at the ordinary temperature (preparative process) or by the hydrolysis of the normal ester in boiling aqueous methyl-alcoholic solution or with boiling *N*/10-hydrochloric acid (preparative method). 3-Methyl 1-hydrogen 4-dimethylaminoisophthalate, colourless, shining leaflets, m. p. 190°, results from the esterification of the acid with methyl alcohol at 140°, from the action of methyl iodide on the normal silver or potassium hydrogen salt, and from the semi-hydrolysis of the normal

ester in methyl-alcoholic solution by means of potassium hydroxide or hydrogen chloride. The constitution of the esters is deduced from the production of the former by the esterification of the acid with methyl alcohol and hydrogen chloride, and from the behaviour of the silver salts when distilled, whereby in the first case a mixture of (?) *p*-dimethylaminobenzoic acid, m. p. 230—233°, and methyl *p*-dimethylaminobenzoate is produced, whilst in the second instance, resinous and less definite substances are formed, which could not be fully examined owing to lack of material. The experiment, however, proves that the two silver salts behave in a totally dissimilar manner when heated, and that a transformation only occurs to a slight extent if at all.

H. W.

### Esterification of Unsymmetrical Di- and Poly-basic Acids.

**XXX. Esterification of 4-Acetylaminoisophthalic Acid.** HERMANN MEYER (*Monatsh.*, 1920, **41**, 125—138. Compare Wegscheider, Malle, Ehrlich, and Skutezky, A., 1919, i, 76, and preceding abstract).—1-Methyl 3-hydrogen 4-acetylaminoisophthalate, m. p. 218°, is prepared by the semi-hydrolysis of the normal ester with alkali in aqueous or methyl-alcoholic solution. The isomeric 3-methyl 1-hydrogen 4-acetylaminoisophthalate, m. p. 265°, is obtained by the action of methyl iodide on the normal silver salt in the presence of methyl alcohol (the process does not, however, occur smoothly, and yields only 20% of the normal ester, a small amount of the hydrogen ester, and mainly the unchanged acid), or on the potassium hydrogen salt (in which case also side-reactions occur, giving rise to free acid). A hydrogen ester could not be isolated from the products of the action of methyl alcohol on the acid at 100° or 120—130° or 200°, since under these conditions loss of carbon dioxide appears to take place with consequent formation of *p*-acetylaminobenzoic acid. Similarly, the hydrogen ester could not be obtained by boiling the normal ester with dilute aqueous hydrochloric acid. The constitution of the esters follows from the observation that the isomeride, m. p. 218°, is transformed by boiling acetic anhydride into methyl anhydro-4-acetylaminoisophthalate, m. p. 172°, and since dehydration occurs by loss of water between the acetylmino- and the adjacent carboxyl group the ester must be the 1-methyl compound.

Silver 4-acetylaminoisophthalate forms a gelatinous mass; a silver hydrogen salt could not be isolated. Potassium hydrogen 4-acetylaminoisophthalate is prepared by the addition of aqueous potassium hydroxide solution to a suspension of the acid in methyl alcohol.

H. W.

### Esterification of Unsymmetrical Di- and Poly-basic Acids.

**XXXI. Esterification of 4-Methylaminoisophthalic Acid.** JOHANN TAUB (*Monatsh.*, 1920, **41**, 139—152. Compare Wegscheider, Malle, Ehrlich, and Skutezky, A., 1919, i, 76, and preceding abstracts).—1-Methyl 3-hydrogen 4-methylaminoisophthalate, colourless, delicate needles, m. p. 244—245° (decomp.), is formed in

larger quantity than the isomeric 3-methyl 1-hydrogen 4-methyl-aminoisophthalate by all the methods of esterification and semi-hydrolysis; the latter, colourless crystals, m. p. 220—221°, is prepared by the semi-hydrolysis of the normal ester or by the action of methyl iodide on the silver salt. The former isomeride seems to be the only one produced by the action of methyl-alcoholic hydrogen chloride or sulphuric acid on the acid; in the absence of mineral acid, methyl alcohol only causes slight esterification of 4-methyl-aminoisophthalic acid at 100°, whilst at 170° no trace of ester is produced, the acid losing carbon dioxide and being converted into an anthraquinone dye, which was not further investigated. The action of methyl iodide on the *potassium hydrogen* salt in the presence of methyl alcohol yields mainly the acid, together with small quantities of the normal ester and the 1-methyl 3-hydrogen ester, whilst a mixture of acid, normal ester, 1- and 3-methyl hydrogen esters (in which the former considerably predominates), is obtained from the *silver hydrogen* salt; the methylamino-group does not appear to undergo methylation during this treatment. The hydrolysis of the normal ester with methyl-alcoholic potassium hydroxide, aqueous potassium hydroxide, water, and with aqueous or methyl-alcoholic hydrochloric acid under varied conditions is described; in every case the hydrogen ester consists mainly of the 1-methyl compound, the 3-methyl isomeride being formed in subordinate amount if at all.

H. W.

### Esterification of Unsymmetrical Di- and Poly-basic Acids.

#### XXXII. 4-Nitroisophthalic Acid and the Reduction of its Hydrogen Esters to 4-Aminoisophthalic Esters.

PHILIPP AXER (*Monatsh.*, 1920, **41**, 153—165).—The oxidation of 4-nitro-m-xylene by calcium permanganate leads to the formation of a mixture of 4-nitroisophthalic acid, m. p. 255—256·5° (corr.), 6-nitro-m-toluic acid, yellow, silky needles, m. p. 218·5—219°, and small quantities of 4-nitro-m-toluic acid, m. p. 133—134·5°. *Potassium hydrogen 4-nitroisophthalate* is readily prepared as a white powder, sparingly soluble in water, by the mixture of solutions of equivalent amounts of the normal potassium salt and the free acid; the silver hydrogen compound could not be prepared. *Methyl 4-nitroisophthalate*, yellow, rhombic crystals,  $a:b:c=0\cdot3875:0\cdot3383:1$ , m. p. 87—88·5°, is prepared in about 80% yield by the esterification of the acid with a mixture of equal volumes of concentrated sulphuric acid and methyl alcohol. *1-Methyl 3-hydrogen 4-nitroisophthalate*, well-formed, colourless needles, m. p. 153·5—154° (corr.), is most conveniently prepared from the acid and methyl alcohol in the presence of a smaller proportion of concentrated sulphuric acid, and its constitution is deduced from its mode of formation. It is also obtained from the acid and methyl alcohol at 100° in the absence of mineral acid. *3-Methyl 1-hydrogen 4-nitroisophthalate*, powder, m. p. 192—194° (corr.), is most conveniently prepared by the semi-hydrolysis of the normal ester either by potassium hydroxide in aqueous methyl-alcoholic solution or by aqueous methyl-

alcoholic hydrogen chloride. Potassium hydrogen 4-nitroisophthalate is not methylated by treatment with methyl iodide at 100° during twenty hours. The acid is partly transformed by methyl iodide in the presence of acetone and silver oxide into the normal ester, but remains unaffected by methyl sulphate. The silver salt is quantitatively transformed by methyl iodide into the normal ester.

1-Methyl 3-hydrogen 4-nitroisophthalate is reduced by tin and concentrated hydrochloric acid to 1-methyl 3-hydrogen 4-aminoisophthalate, m. p. 221—222° (corr.), the yield, however, being poor, and the product contaminated with much free amino-acid. Better results are obtained with the isomeric ester, which yields 3-methyl 1-hydrogen 4-aminoisophthalate, colourless, crystalline powder, m. p. 228—230° (corr., slight decomp.). Methyl 4-aminoisophthalate, m. p. 127—129° (corr.), is similarly obtained in good yield from the normal nitro-ester.

H. W.

### Esterification of Unsymmetrical Di- and Poly-basic Acids. XXXIII. Esterification of Aminodicarboxylic Acids.

RUDOLF WEGSCHEIDER (*Monatsh.*, 1920, **41**, 167—183).—A theoretical paper which is devoted to a discussion of the results obtained during the investigation of the esterification of aminocarboxylic acids and the partial hydrolysis of their esters.

The aminodicarboxylic acids and, so far as is known, other dicarboxylic acids which contain an imino-group or nitrogen atom as a member of an open chain generally conform to the rules which have been propounded for the formation of hydrogen esters. The amino-groups must be assumed to cause steric hindrance, the unsubstituted or alkylated amino-groups to have a positive and the acylated amino-groups to have a negative action. Less regularity is observed in the semi-hydrolysis; it not infrequently happens that the action follows different courses in alcoholic and aqueous solution, but, on the other hand, it is immaterial whether hydrolysis is effected by alkali hydroxide or by hydrochloric acid. In the semi-hydrolysis of the acylated amino-esters, the influence of the strength of the carboxyl group outweighs that of steric hindrance; on the other hand, these two factors do not appear adequate to explain the course of semi-hydrolysis of the esters of unsubstituted or *N*-alkylated amino-acids, particularly in aqueous solution. With regard to the other reactions, irregularities are only observed with dimethylaminoisophthalic acid (action of alcohol on the acid in the absence of catalyst and of methyl iodide on the salts). It is quite possible that all these irregularities (including such as are observed during semi-hydrolysis) are to be ascribed to the participation of the amino-groups in the reactions.

The following generalisations (which are not without exception) are drawn from a consideration of the melting points of amino-iso- and terephthalic acids and their esters: (1) Methylation at the nitrogen atom depresses the melting point (exceptions occur in the methylation of methylaminoterephthalic acid, 1-methyl

3-hydrogen 4-aminoisophthalate, and acetylaminoisophthalic acid). (2) Acetylation at the nitrogen atom raises the melting point of those hydrogen esters in which the esterified carboxyl is in the ortho-position to the amino-group, but depresses it in the case of the acids (except methylaminoisophthalic acid), and to a slight extent in that of the acid esters of different relative position, as well as in the instances of the dimethyl esters of aminoisophthalic acid and methylaminoterephthalic acid. (3) Derivatives of 4-aminoisophthalic acid have higher melting points than the corresponding compounds derived from aminoterephthalic acid. (The dimethyl esters of the amino- and acetylamino-acids form exceptions.) (4) Among isomeric hydrogen esters of acetylated acids, the compound in which the esterified carboxyl group is adjacent to the acetylamino-group has the higher melting point; a similar irregularity is not observed with the amino- and methylamino-acids.

H. W.

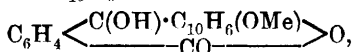
**Friedel and Crafts' Reaction: Nitrophthalic Anhydrides and Acetylaminoisophthalic Anhydrides with Benzene and Aluminium Chloride.** WALTER A. LAWRENCE (*J. Amer. Chem. Soc.*, 1920, **42**, 1871—1879).—3-Nitrophthalic anhydride, when heated with benzene and aluminium chloride, gave a mixture of *o'*-nitro-*o*-benzoylbenzoic acid, m. p. 220—221° (decomp.), and *m*-nitro-*o*-benzoylbenzoic acid, m. p. 157—160° (decomp.). 2-Ethyl 1-hydrogen 3-nitrophthalate gave with thionyl chloride an acid chloride, m. p. 76—77°, which with benzene and aluminium chloride yielded *o'*-nitro-*o*-benzoylbenzoic acid. Similarly the chloride of 1-ethyl 2-hydrogen 3-nitrophthalate gave *m*-nitro-*o*-benzoylbenzoic acid. 4-Nitrophthalic anhydride when submitted to Friedel and Crafts' reaction gave *m*-nitro-*o*-benzoylbenzoic acid and *p*-nitro-*o*-benzoylbenzoic acid. Under similar conditions, 3-acetylaminoisophthalic anhydride yielded *m*-amino-*o*-benzoylbenzoic acid, m. p. 193—194°, and *o'*-amino-*o*-benzoylbenzoic acid, m. p. 159—160°, together with some *diphenyl-?aminophthalide*, m. p. 86—89°. 4-Acetylaminoisophthalic anhydride gave *m*-amino-*o*-benzoylbenzoic acid and *p*-amino-*o*-benzoylbenzoic acid.

W. G.

**$\alpha$ -Naphtholphthaleins and its Ethers.** W. SCHULENBERG (*Ber.*, 1920, **53**, [B], 1445—1457).—As considerable doubt exists as to the constitution of the  $\alpha$ -naphtholphthalein obtained by the condensation of phthalyl chloride with  $\alpha$ -naphthol (compare Sørensen and Palitzsch, A., 1910, ii, 446; Copisarow and Weizmann, T., 1915, **107**, 878; Csányi, this vol., i, 54), the author has attempted the synthesis of an undoubted *oo'*-naphtholphthalein, and for this purpose has condensed  $\alpha$ -naphtholphthaloylic acid (Deichler and Weizmann, A., 1903, i, 349) with  $\alpha$ -naphthol in sulphuric acid solution; the product forms colourless crystals, m. p. 253—254° after previous darkening, and closely resembles the substance described by Csányi as the *pp'*-isomeride, but differs widely from the *oo'*-derivative described by Copisarow and Weizmann, to which the m. p. 209—210° is ascribed. The mode of attachment of the second naphthol group is elucidated by the conversion of

the substance into  $\alpha$ -naphthafluoran. The same substance was also obtained in small yield by the interaction of phthalyl chloride and  $\alpha$ -naphthol under milder conditions than those usually adopted, whilst no trace of an isomeric *p*-phthalein could be detected.

The condensation of phthalic acid with  $\alpha$ -naphthyl ethers follows a different course. Thus phthalic anhydride and  $\alpha$ -naphthyl methyl ether react in carbon disulphide solution in the presence of aluminium chloride to yield 4-methoxynaphthylphthaloylic acid, colourless, acute prisms, m. p.  $194^{\circ}$  (the sodium salt, rhombic plates, and calcium salt, prisms,  $+10\text{H}_2\text{O}$ , are described), which can also be prepared from phthalyl chloride and  $\alpha$ -naphthyl methyl ether. The constitution of the acid is deduced from the extreme difficulty of effecting its demethylation, and, with greater certainty, from a comparison of its properties with those of the isomeric acid of the ortho-series. Thus the former yields a *normal* and a *pseudo-methyl* ester, colourless, rhombic plates, m. p.  $96^{\circ}$ , and needles, m. p.  $120^{\circ}$ , whilst the latter gives an *ether* ester, double pyramids, m. p.  $117$ – $119^{\circ}$ , and an *ether acid*, colourless needles, m. p.  $179^{\circ}$ . Finally, when melted with potassium hydroxide, the acid yields 1:4-hydroxynaphthoic acid, m. p.  $178^{\circ}$ . 4-Methoxynaphthylphthaloylic acid behaves as a weak acid, and is partly liberated from its sodium salt by carbon dioxide, and cannot be titrated with sodium hydroxide in the presence of phenolphthalein as indicator; its behaviour indicates its existence in the desmotropic forms,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_{10}\text{H}_6\cdot\text{OMe}$  and



and this conception is supported by the isolation of the two methyl esters mentioned above. It suffers extensive decomposition when heated above its melting point, yielding, among other substances,  $\alpha$ -naphthyl methyl ether, phthalic acid,  $\alpha$ -naphthafluoran, and a substance, pale yellow, hexagonal prisms, m. p.  $201$ – $202^{\circ}$ , which was not further identified. It condenses with  $\alpha$ -naphthyl methyl ether in the presence of concentrated sulphuric acid to give *p*-naphtholphthalein dimethyl ether, colourless, slender needles, m. p.  $246$ – $247^{\circ}$ , which can also be obtained in 83% yield by the prolonged interaction of phthalyl chloride and  $\alpha$ -naphthyl methyl ether in carbon disulphide solution in the presence of a trace of aluminium chloride at the ordinary temperature. The isomeric *o*-naphtholphthalein dimethyl ether is prepared by methylation of the phthalein, and forms colourless, microscopic needles, m. p.  $291^{\circ}$ .

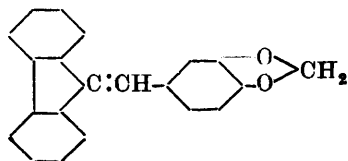
The results outlined above do not appear to harmonise readily with those obtained by Copisarow and Weizmann (*loc. cit.*), who find that the action of phthalyl chloride on  $\alpha$ -naphthyl ethyl ether produces, successively, *o*-1-ethoxynaphthoylbenzoic acid, m. p.  $155$ – $156^{\circ}$ , and di-1-ethoxynaphthylphthalide, m. p.  $159^{\circ}$ . The author has therefore repeated the work, and has obtained totally different results, since he finds the acid to melt at  $166$ – $167^{\circ}$  and to have all the properties of a para-derivative, since it behaves

towards concentrated sulphuric acid in precisely the same manner as 4-methoxynaphthylphthaloylic acid, and is converted by fused potassium hydroxide into 4-hydroxynaphthoic acid. Further, the naphtholphthalein ethyl ether did not melt below 298°, whilst the acid was indifferent towards dealkylating agents. 1:2-Naphtholphthaloylic acid can be readily converted into *o*-1-ethoxynaphthoylbenzoic acid, irregular prisms, m. p. 145°, by treatment with ethyl sulphate and subsequent hydrolysis of the ethyl ester, prisms, m. p. 89°, thus produced. H. W.

**Synthesis of 3:5-Dihydroxybenzaldehyde.** F. MAUTHNER (*J. pr. Chem.*, 1920, [ii], 101, 93—96).—3:5-Dimethylcarbonatobenzaldehyde, m. p. 154—155°, is prepared by the action of hydrogen on a solution of 3:5-dimethylcarbonatobenzoyl chloride (E. and H. O. L. Fischer, A., 1913, i, 478) in dry toluene at 110° in the presence of palladised barium sulphate. It yields a *p*-nitrophenylhydrazone, red needles, m. p. 222—223°, and is converted by aqueous sodium hydroxide and subsequent acidification into 3:5-dihydroxybenzaldehyde, colourless needles, m. p. 145—146°; the *p*-nitrophenylhydrazone, which completely decomposes, without melting, at 280°, and the semicarbazone, long needles, m. p. 223—224° (decomp.), of the latter are described. H. W.

**Preparation of Piperonaldehyde from Camphor Oil.** I. and II. SHOICHIRO NAGAI (*J. Chem. Ind. Tokyo*, 1920, 23, 56—79, 151—172).—The fraction of camphor oil, b. p. 220—230°, contains mainly safrole, eugenol, carvacrol, cadinene, and *n*-octoic acid. By further distillation of this fraction, treatment with 25% sodium hydroxide, cooling at -19°, and adding a few crystals of safrole, safrole could be completely crystallised out. Next, when 300 c.c. of safrole are heated with 45 grams of potassium hydroxide (15 grams in each 100 c.c.) for five hours at 180—200°, 90% was changed into isosafrole. The method of oxidation of isosafrole into piperonaldehyde is discussed. Potassium dichromate and sulphuric acid gave the best yield, 47% of the theoretical value. When potassium permanganate was used, the yield was only 8%, most of the isosafrole being oxidised to piperonylic acid. The purification of piperonaldehyde is best effected by recrystallisation from 70% alcohol. CHEMICAL ABSTRACTS.

**New Reaction of Aldehydes.** REMO DE FAZI (*Gazzetta*, 1920, 50, ii, 146—148. Compare A., 1916, ii, 457; Guglielmelli and Delmon, A., 1918, i, 161).—Since fluorene resembles acenaphthene



in giving a reddish-violet coloration with cyclic aldehydes in presence of concentrated sulphuric acid, the author has initiated experiments to ascertain if the condensation products of fluorene with aldehydes are able to yield this coloration with the sulphuric acid. It is



found that, in presence of sodium ethoxide, fluorene condenses at the ordinary temperature with piperonaldehyde, *m*-tolualdehyde, cuminaldehyde, *p*-dimethylaminobenzaldehyde, etc.; for instance, with piperonaldehyde, fluorene yields piperonylidenefluorene (foregoing formula). These condensation products, to be described in detail later, give the above coloration in alcoholic solution with concentrated sulphuric acid.

T. H. P.

### Constitution of the Salts of Aminoacetophenones.

MITSURU KUHARA, HEIKICHI SAITO, and AKIRA SHIMOMURA (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 201—215).—A study of the absorption spectra of the different salts of the three isomeric aminoacetophenones. The hydrochlorides of *o*- and *p*-aminoacetophenones both give coloured solutions in alcohol, and these coloured salts show a new absorption band in the visible region. This coloration is weakened if an excess of dry hydrogen chloride is passed through the alcoholic solution, and then the second band is no longer visible. *m*-Aminoacetophenone hydrochloride and *p*-dimethylaminoacetophenone hydrochloride do not give coloured salts, and their alcoholic solutions do not give an extra absorption band. It is considered that the coloured ortho- and para-salts are the quinonoid form and the colourless salts the benzenoid form, the change from one form to the other being of the keto-enol type.

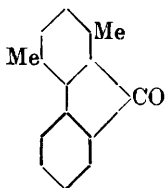
*p*-Dimethylaminoacetophenone, m. p. 105°, was prepared by heating *p*-aminoacetophenone and methyl iodide in aqueous sodium hydroxide for several hours. It gave a *hydrochloride*, m. p. 147—148° (decomp.), and a *picrate*, m. p. 124° (decomp.).

W. G.

### Preparation of 1:4-Dimethylfluorenone and Attempts to Transform it into a Derivative of Phenanthrone.

ALFRED SCHAARSCHMIDT and JOHANN HERZENBERG (*Ber.*, 1920, **53**, [B], 1388—1398. Compare Schaarschmidt, A., 1917, i, 275).—Various attempts to synthesise *o*-aminophenyl *p*-xylyl ketone are described. Thus, 2-*p*-toluenesulphonylaminophenyl *p*-xylyl ketone,  $C_6H_3Me_2 \cdot CO \cdot C_6H_4 \cdot NH \cdot SO_2 \cdot C_6H_4Me$ , small, colourless crystals, m. p. 107—108°, was prepared by the successive action of phosphorus pentachloride and aluminium chloride on *p*-toluenesulphonylanthranilic acid in the presence of *p*-xylene, but the *p*-toluenesulphonyl group could not be smoothly removed. Similarly, *p*-xyloyl-*o*-benzoic acid was converted successively into the chloride and *amide*, colourless needles, m. p. 149—150°, which could not be transformed into the amine in a satisfactory manner. Attempts to prepare *o*-nitrophenyl *p*-xylyl ketone by the action of *o*-nitrobenzoyl chloride on *p*-xylene in the presence of aluminium chloride and carbon disulphide were unsuccessful, resinous products being obtained. Finally, *o*-bromophenyl *p*-xylyl ketone, colourless, shining leaflets, m. p. 46°, was converted by alcoholic ammonia at 180—190° into *o*-aminophenyl *p*-xylyl ketone, mainly obtained as a yellow oil which decomposed completely when distilled; from

this, however, small amounts of pale yellow crystals, m. p. 76—78° to a cloudy liquid, which suddenly became transparent at 88—90°, could be isolated. It was converted by diazotisation and subsequent treatment with copper powder into *o*-hydroxyphenyl *p*-xylyl ketone (yellowish-brown, viscous mass, which was not further investigated), 2:5-dimethylbenzophenone, b. p. 312—314°/atmospheric pressure, and 1:4-dimethylfluorenone (annexed formula), long, yellow needles, m. p. 108°. When fused with potassium hydroxide, the latter yields an acid, colourless needles, m. p. 145° (the silver salt is described), which, since it is not esterified by cold saturated methyl-alcoholic hydrogen chloride, and yields 1:4-dimethylfluorenone when treated with concentrated sulphuric acid, is considered to be 2:5-dimethyldiphenyl-6-carboxylic acid.



The fission of substituted ring ketones under the influence of molten alkali hydroxide appears to take place quantitatively in one direction only, and the position occupied by the carboxyl group depends on the substituent already present. If the latter is acidic in character, the new carboxyl group becomes located in the unsubstituted benzene nucleus; if, however, it is basic ( $-\text{NH}_2$  or  $-\text{OH}$ ), the new group is attached to the already substituted nucleus. The latter seems also to be the case when a methyl radicle is in the ortho-position.

H. W.

**Anthracene. VI. Desmotropy of the Reduction Products of Hydroxyanthraquinones.** KURT H. MEYER and ALBERT SANDER (*Annalen*, 1920, **420**, 113—125. Compare A., 1911, i, 193). An investigation of the effect of the introduction of hydroxy-groups on the equilibrium between anthrone and anthranol forms.

The reduction of 1-hydroxyanthraquinone to a substance considered to be 1-hydroxyanthranol has been described by the Höchst Farbwerke (D.R.-P. 242053); the absence of fluorescence from the alcoholic solution and failure of the substance to combine with bromine show it to be in reality 1-hydroxyanthrone, and this conception explains the observed ability of the compound to condense with isatin chloride or anilide, with the production of indigoid dyes containing the new group in the side nucleus. In alcoholic solution, equilibrium is attained in the presence of 3—4% of hydroxyanthranol. With 1:9-dihydroxyanthrone and 1-hydroxyanthraquinol, equilibrium is set up when about 10% of the latter is present. In the cases of 1:4-dihydroxyoxanthrone and 1:4-dihydroxyanthraquinol, the latter is found to pass with great readiness into the former, so that it appears, in general, that the tendency towards ketone formation is increased by the entrance of hydroxyl groups in the  $\alpha$ -position in the side nucleus.

The following individual substances are described: 1:9-anthr-  
anylene diacetate,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{OAc}) \\ \text{CH} \end{smallmatrix} \text{C}_6\text{H}_3(\text{OAc})$ , colourless or pale  
yellow needles, m. p. 148—149°; the dibenzoate, yellow

f f\*

needles, m. p.  $191^{\circ}$  (from  $\alpha$ -hydroxyanthrone and the requisite acid chloride in the presence of pyridine); 9-bromo-1-hydroxyanthrone,  $\text{C}_6\text{H}_4\langle\text{CH}(\text{OH})\text{CO}\rangle\text{C}_6\text{H}_3\cdot\text{OH}$ , yellow needles, m. p.  $273^{\circ}$  (decomp.) after softening and darkening from  $130^{\circ}$ , which readily loses hydrogen bromide, and, on treatment with copper powder, gave a substance, m. p.  $188\text{--}189^{\circ}$ ; 1:9-dihydroxyanthrone,  $\text{C}_6\text{H}_4\langle\text{CH}(\text{OH})\text{CO}\rangle\text{C}_6\text{H}_3\cdot\text{OH}$ , deep yellow needles, m. p.  $135\text{--}137^{\circ}$  (from the bromo-compound and aqueous acetone); 1-hydroxyanthraquinol, dark olive-green needles, m. p.  $204\text{--}206^{\circ}$ , which undergoes autoxidation with extreme ease; 1:4:9-trihydroxyanthrone,  $\text{C}_6\text{H}_4\langle\text{CH}(\text{OH})\text{CO}\rangle\text{C}_6\text{H}_2(\text{OH})_2$ , m. p.  $157\text{--}158^{\circ}$  after previous softening, which is best obtained by reducing a solution of quinizarin in glacial acetic acid with tin and hydrochloric acid, and which has been considered by Liebermann to be 1:4-dihydroxyanthraquinol; the latter substance, prepared by reduction of quinizarin with zinc dust in alkaline solution and subsequent acidification, has m. p.  $131\text{--}136^{\circ}$ , readily undergoes autoxidation, passes into the ketonic form when recrystallisation is attempted, and is oxidised by an alcoholic solution of bromine to quinizarin.

Purpurin, when subjected to reduction, is converted into leucopurpurin and a substance,  $\text{C}_{14}\text{H}_{10}\text{O}_5$ , m. p.  $162\text{--}163^{\circ}$ , which is transformed in alkaline solution into quinizarin, and has hence been termed leucoquinizarin I. It is now shown that it is produced when leucopurpurin is boiled in acetic acid solution, that it is stable towards air and indifferent to an alcoholic solution of bromine, and, further, that its conversion into quinizarin by sodium hydroxide occurs in complete absence of air. It therefore appears to be 2-hydroxy-1:4-diketo-1:2:3:4-tetrahydroanthraquinol, and to be formed by the passage of leucopurpurin into the ketonic form, the subsequent production of quinizarin being due to the loss of water.

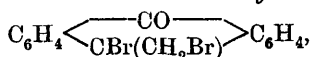
Liebermann's  $\beta$ -hydroxyanthranol has been further examined, but definite conclusions as to the desmotropic relationships cannot yet be drawn; the stable modification, however, appears to be enolic.

H. W.

**Anthracene. VII. The Alkylation of Anthranol.** KURT H. MEYER and HANS SCHLÖSSER (*Annalen*, 1920, **420**, 126—133).—In continuation of previous work (A., 1911, i, 195), the authors have studied the alkylation of anthranol by alkyl sulphates and alkyl haloids respectively. The former shows the greater tendency towards the formation of O-ethers by direct exchange of the alkyl group for the metallic atom, whereas the latter cause alkylation in the nucleus to a much more pronounced extent. It is suggested that a part of the alkyl haloid is added at the active double bond of anthranol, yielding 9-alkylanthrone, which is transformed in the alkaline solution into 9-alkylanthranol; the latter can then react

further with alkyl haloid, one portion of it giving the O-ether, whilst another portion adds alkyl haloid and yields dialkylanthrone.

*Anthranol methyl ether*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C(OMe)} \\ | \\ \text{CH} \end{smallmatrix} \text{C}_6\text{H}_4$ , coarse leaflets, m. p.  $94^\circ$ , is prepared by the action of methyl sulphate and alkali on an alcoholic solution of anthrone; when dissolved in boiling benzene and treated with phosphorus pentachloride, it yields 10-chloroanthranol methyl ether, yellow crystals, m. p.  $154^\circ$ , whilst with bromine in carbon disulphide solution it gives 10-bromoanthranol methyl ether, colourless crystals, m. p.  $145^\circ$ . When treated with aqueous potassium hydroxide and methyl iodide, anthrone is mainly converted into methylanthranol methyl ether,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C(OMe)} \\ | \\ \text{CMe} \end{smallmatrix} \text{C}_6\text{H}_4$ , m. p.  $147^\circ$ , together with very small quantities of dimethylanthrone, m. p.  $95^\circ$ , which, according to the older observations of Hallgarten, is the main product of the change. Methylanthranol methyl ether is transformed by bromine in carbon disulphide solution into  $\omega$ -9-dibromomethylanthrone,



yellow crystals, m. p.  $135\text{--}140^\circ$  (decomp.) after darkening at  $120^\circ$ , the constitution of which is deduced from its formation from methyleneanthraquinone and bromine (following abstract).

With ethyl sulphate and alkali, anthrone gives *anthranol ethyl ether*, yellow plates, m. p.  $73^\circ$ , which yields a very unstable bromoderivative, and is converted by amyl nitrite in acetic acid solution containing a little hydrochloric acid into anthraquinoneoxime. In agreement with Goldmann's data, anthranol is converted by ethyl iodide into diethylanthrone, m. p.  $135^\circ$ , and 9-ethylanthranol ethyl ether, m. p.  $84^\circ$ .

Anthrone is transformed by aqueous methylamine solution into N-methylmesoanthramine,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C(NHMe)} \\ | \\ \text{CH} \end{smallmatrix} \text{C}_6\text{H}_4$ , sulphur-yellow needles, m. p.  $90^\circ$  after softening at  $85^\circ$ ; the *hydrochloride* forms pale yellow crystals, m. p.  $225^\circ$ . The action of methyl iodide on the base gives only unchanged material and anthraquinone, whilst the latter is obtained when methyl sulphate is used. H. W.

**Anthracene. VIII. Methyleneanthraquinone.** KURT H. MEYER (*Annalen*, 1920, **420**, 134—136).—Simple methylenequinones have been somewhat frequently described in the literature, but several of them have been shown by Pummerer and Cherbuliez (A., 1915, i, 419) to be dehydrophenols, whilst, more recently (A., 1919, i, 439), Pummerer has expressed the opinion that the remainder are more complex substances, which are probably also to be regarded as dehydrophenols. The author has now succeeded in isolating *methyleneanthraquinone*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{:CH}_2) \end{smallmatrix} \text{C}_6\text{H}_4$ , by the condensation of a cold alkaline solution of anthranol with an excess of form-aldehyde. It forms stable, pale yellow prisms, m. p.  $148^\circ$ , and

instantaneously adds bromine in carbon disulphide solution, yielding bromomethylbromoanthrone, m. p. 135—140° (decomp.) after becoming discoloured at 110°, identical with the product obtained by the bromination of methylanthranol methyl ether (preceding abstract). H. W.

**Rotatory Dispersion of the Menthyl Esters of certain Keto-acids.** H. RUPE and H. KÄGI (*Annalen*, 1920, 420, 33—84).—The present communication describes an extension of the work of Rupe and Lenzinger (A., 1913, i, 266, 884), who prepared a number of the esters, but only observed their specific rotations for the sodium *D*-line. The rotatory dispersions are now recorded. The following substances are described.

Menthyl cyanoacetate, m. p. 83·5°,  $[\alpha]_C^{20} - 64\cdot15^\circ$ ,  $[\alpha]_D^{20} - 80\cdot92^\circ$ ,  $[\alpha]_{Hg}^{20} - 95\cdot21^\circ$ ,  $[\alpha]_F^{20} - 123\cdot57^\circ$  in benzene solution. Menthyl phenylpropionate, m. p. 63—64°,  $[\alpha]_C^{20} - 57\cdot31^\circ$ ,  $[\alpha]_D^{20} - 72\cdot56^\circ$ ,  $[\alpha]_{Hg}^{20} - 85\cdot9^\circ$ ,  $[\alpha]_F^{20} - 111\cdot92^\circ$  in benzene. Menthyl ethylacetoacetate,  $[\alpha]_C^{20} - 50\cdot59^\circ$ ,  $[\alpha]_D^{20} - 63\cdot85^\circ$ ,  $[\alpha]_{Hg}^{20} - 75\cdot60^\circ$ ,  $[\alpha]_F^{20} - 98\cdot39^\circ$ . *Menthyl diethylacetoacetate*. b. p. 161°/9·5 mm.,  $D_4^{20} 0\cdot9638$ ,  $[\alpha]_C^{20} - 44\cdot35^\circ$ ,  $[\alpha]_D^{20} - 55\cdot68^\circ$ ,  $[\alpha]_{Hg}^{20} - 65\cdot53^\circ$ ,  $[\alpha]_F^{20} - 84\cdot35^\circ$  in substance,  $[\alpha]_C^{20} - 40\cdot39^\circ$ ,  $[\alpha]_D^{20} - 50\cdot77^\circ$ ,  $[\alpha]_{Hg}^{20} - 59\cdot46^\circ$ ,  $[\alpha]_F^{20} - 76\cdot50^\circ$  in benzene. *Menthyl isopropylacetoacetate* (from menthyl sodioacetoacetate and isopropyl iodide in the presence of toluene at 120—125°), b. p. 158—159°/9 mm.,  $D_4^{20} 0\cdot9603$ ,  $[\alpha]_C^{20} - 48\cdot69^\circ$ ,  $[\alpha]_D^{20} - 61\cdot53^\circ$ ,  $[\alpha]_{Hg}^{20} - 72\cdot91^\circ$ ,  $[\alpha]_F^{20} - 95\cdot05^\circ$  in substance,  $[\alpha]_C^{20} - 47\cdot32^\circ$ ,  $[\alpha]_D^{20} - 59\cdot74^\circ$ ,  $[\alpha]_{Hg}^{20} - 70\cdot58^\circ$ ,  $[\alpha]_F^{20} - 91\cdot70^\circ$  in benzene. *Ethyl diphenylmethylacetoacetate*,  $CH_3\cdot CO\cdot CH(C_6H_5)_2\cdot CO_2Et$ , small, shining rods, m. p. 89—90°. Menthyl diphenylmethylacetoacetate could not be obtained from menthol and the ethyl ester or from menthyl acetoacetate and diphenylbromomethane and alcoholic sodium ethoxide. Reaction could be caused to occur between menthyl sodioacetoacetate and diphenylbromomethane in the presence of dry benzene, giving a product which is resolved into diastereoisomerides by prolonged fractionation; *l*-menthyl *d*-diphenylmethylacetoacetate has m. p. 118°,  $[\alpha]_C^{20} - 33\cdot83^\circ$ ,  $[\alpha]_D^{20} - 41\cdot94^\circ$ ,  $[\alpha]_{Hg}^{20} - 48\cdot18^\circ$ ,  $[\alpha]_F^{20} - 60\cdot00^\circ$ , whilst *l*-menthyl *l*-diphenylmethylacetoacetate has m. p. 90°,  $[\alpha]_C^{20} - 51\cdot13^\circ$ ,  $[\alpha]_D^{20} - 65\cdot15^\circ$ ,  $[\alpha]_{Hg}^{20} - 78\cdot04^\circ$ ,  $[\alpha]_F^{20} - 103\cdot94^\circ$ , and *l*-menthyl *dl*-diphenylmethylacetoacetate has  $[\alpha]_C^{20} - 42\cdot62^\circ$ ,  $[\alpha]_D^{20} - 53\cdot69^\circ$ ,  $[\alpha]_{Hg}^{20} - 63\cdot31^\circ$ ,  $[\alpha]_F^{20} - 82\cdot43^\circ$ . The rotatory dispersion curves of the diastereoisomerides differ widely from one another, and the *d* + *l*-form exhibits complex anomaly. Somewhat similar experiences are encountered with the benzylacetoacetic esters (compare Rupe and Lenzinger, *loc. cit.*); the most readily isolable ester is *l*-menthyl *l*-benzylacetoacetate, m. p. 68°,  $[\alpha]_C^{20} - 94\cdot05^\circ$ ,  $[\alpha]_D^{20} - 121\cdot21^\circ$ ,  $[\alpha]_{Hg}^{20} - 145\cdot67^\circ$ ,  $[\alpha]_F^{20} - 196\cdot73^\circ$ , whilst *l*-menthyl *dl*-benzylacetoacetate, m. p. 48—51°,  $[\alpha]_C^{20} - 43\cdot43^\circ$ ,  $[\alpha]_D^{20} - 55\cdot10^\circ$ ,  $[\alpha]_{Hg}^{20} - 65\cdot20^\circ$ ,  $[\alpha]_F^{20} - 85\cdot85^\circ$ , is also obtained; the *d*-ester could not be isolated in the pure condition. *l*-Menthyl benzylideneacetoacetate (from benzaldehyde and *l*-menthyl acetoacetate in the presence of hydrogen chloride, thus giving the *hydrochloride*, needles, m. p. 118°, as intermediate product) has  $[\alpha]_C^{20} - 8\cdot17^\circ$ ,  $[\alpha]_D^{20} - 10\cdot97^\circ$ ,  $[\alpha]_{Hg}^{20} - 13\cdot66^\circ$ ,  $[\alpha]_F^{20} - 21\cdot27^\circ$  in benzene solution. *l*-Menthyl diacetylacetoacetate, colourless, odourless oil, b. p. 172—173°/

11 mm.,  $D_4^{20}$  1.0239 (the pale blue *copper* salt was analysed), has  $[\alpha]_C^{20} - 61.49^\circ$ ,  $[\alpha]_D^{20} - 79.56^\circ$ ,  $[\alpha]_{Hg}^{20} - 96.34^\circ$ ,  $[\alpha]_F^{20} - 131.32^\circ$  in substance,  $[\alpha]_C^{20} - 51.84^\circ$ ,  $[\alpha]_D^{20} - 66.88^\circ$ ,  $[\alpha]_{Hg}^{20} - 80.68^\circ$ ,  $[\alpha]_F^{20} - 110.64^\circ$  in benzene solution. Attempts to prepare *l*-menthyl benzoylacetate were unsuccessful. Menthyl benzoylacetate has  $[\alpha]_C^{20} - 50.95^\circ$ ,  $[\alpha]_D^{20} - 64.39^\circ$ ,  $[\alpha]_{Hg}^{20} - 76.15^\circ$ ,  $[\alpha]_F^{20} - 99.89^\circ$  in benzene, whilst under similar conditions *l*-menthyl benzoylbenzylideneacetate has  $[\alpha]_C^{20} - 61.75^\circ$ ,  $[\alpha]_D^{20} - 78.62^\circ$ ,  $[\alpha]_{Hg}^{20} - 93.69^\circ$ ,  $[\alpha]_F^{20} - 123.84^\circ$ . Menthyl *l*-benzoylcinnamylacetate,  $CHPh \cdot CH \cdot CH_2 \cdot CHBz \cdot CO_2 \cdot C_{10}H_{19}$  (Rupe and Lenzing, *loc. cit.*), has  $[\alpha]_C^{20} - 67.41^\circ$ ,  $[\alpha]_D^{20} - 86.08^\circ$ ,  $[\alpha]_{Hg}^{20} - 102.18^\circ$ ,  $[\alpha]_F^{20} - 135.71^\circ$ , but the diastereoisomeric ester could not on this occasion be isolated in a sufficiently pure condition for polarimetric investigation. Menthyl *d*-benzoylphenylacetate has  $[\alpha]_C^{20} + 13.73^\circ$ ,  $[\alpha]_D^{20} + 21.10^\circ$ ,  $[\alpha]_{Hg}^{20} + 28.58^\circ$ ,  $[\alpha]_F^{20} + 49.91^\circ$  in benzene,  $[\alpha]_C^{20} - 43.89^\circ$ ,  $[\alpha]_D^{20} - 58.91^\circ$ ,  $[\alpha]_{Hg}^{20} - 75.08^\circ$ ,  $[\alpha]_F^{20} - 93.57^\circ$  in alcohol with one drop of piperidine. The dextrorotation is caused by the activity of the asymmetric complex of the acid preponderating over that of the menthol; in alcoholic solution, however, the ketonic rapidly passes into the enolic form, thus destroying the asymmetry of the carbon atom in the acid portion of the molecule and leaving an activity entirely due to the presence of the menthyl group. Menthyl dibenzoylacetate, colourless needles, m. p.  $138.5-139^\circ$ , has  $[\alpha]_C^{20} - 49.58^\circ$ ,  $[\alpha]_D^{20} - 64.07^\circ$ ,  $[\alpha]_{Hg}^{20} - 76.88^\circ$ ,  $[\alpha]_F^{20} - 104.18^\circ$  in benzene.

The ethyl menthyl acetylsuccinates have also been investigated. The  $\alpha$ -ester,  $CO_2Et \cdot CH_2 \cdot CHAc \cdot CO_2 \cdot C_{10}H_{19}$ , prepared from menthyl acetoacetate and ethyl chloroacetate in the presence of alcoholic sodium ethoxide, has b. p.  $192-195/9$  mm.,  $111-112/0.1$  mm.,  $D_4^{20}$  1.0295,  $[\alpha]_C^{20} - 44.76^\circ$ ,  $[\alpha]_D^{20} - 56.67^\circ$ ,  $[\alpha]_{Hg}^{20} - 67.24^\circ$ ,  $[\alpha]_F^{20} - 87.97^\circ$  in substance,  $[\alpha]_C^{20} - 45.59^\circ$ ,  $[\alpha]_D^{20} - 57.80^\circ$ ,  $[\alpha]_{Hg}^{20} - 67.99^\circ$ ,  $[\alpha]_F^{20} - 89.38^\circ$  in benzene solution; the  $\beta$ -ester,  $CO_2Et \cdot CHAc \cdot CH_2 \cdot CO_2 \cdot C_{10}H_{19}$ , from menthyl chloroacetate and ethyl sodioacetoacetate, is a colourless, viscous oil, b. p.  $200-202/12$  mm.,  $116-117/ca. 0.1$  mm.,  $D_4^{20}$  1.0267,  $[\alpha]_C^{20} - 38.77^\circ$ ,  $[\alpha]_D^{20} - 48.80^\circ$ ,  $[\alpha]_{Hg}^{20} - 57.45^\circ$ ,  $[\alpha]_F^{20} - 74.02^\circ$  in substance,  $[\alpha]_C^{20} - 40.94^\circ$ ,  $[\alpha]_D^{20} - 51.59^\circ$ ,  $[\alpha]_{Hg}^{20} - 61.68^\circ$ ,  $[\alpha]_F^{20} - 78.29^\circ$  in benzene. The product obtained by heating a mixture of menthol and ethyl acetylsuccinate is a mixture of 90% of the  $\alpha$ - with 10% of the  $\beta$ -ester.

The enol content of several menthyl esters has been determined by Meyer's method of titration with bromine. The following percentages of enol are thus found, the figures for the corresponding ethyl esters being placed within brackets: menthyl acetoacetate, 17.37% (7.71%); menthyl ethylacetoacetate, 1.69% (3.1%); menthyl diacetylacetate, 72.72% (90%); menthyl acetylsuccinate, 0.65% (3.7%). Menthyl benzoylacetate and menthyl benzoylphenylacetate do not unite with bromine.

On the basis of the present and previous communications, the authors are led to distinguish four types of abnormal rotatory dispersion: (i) total anomaly of a mixture of two substances with opposed activities (Tschugaev's extramolecular anomalous dispersion); (ii) total anomaly of a compound containing two different asymmetric complexes, one of which is dextro-, the other levo-rotatory (Tschugaev's intramolecular anomalous dispersion); (iii) the

rotatory dispersion curve does not pass through a maximum or minimum, neither does it approximate to a horizontal line, but  $\lambda_a$  and  $\lambda_0^2$  differ widely from the normal values and  $\frac{1}{[\alpha]}\lambda^2$  gives bent or zig-zag lines (complex rotatory dispersion of Lowry and Dixon); (iv) apparently normal course of the curves and  $\frac{1}{[\alpha]}\lambda^2$  gives straight lines, but  $\lambda_a$  and  $\lambda_0^2$  differ greatly (at least  $\pm 15 \mu\mu$  for the former) from the normal value for the particular class of compound (relative anomaly).

The paper contains a criticism of the proposal by Lowry and Abram (T., 1919, 115, 300) to delete the "relatively abnormal" classification; the author considers that sufficient substances are known, in which  $\lambda_a$  differs by 15—60  $\mu\mu$  and  $\lambda_0^2$  by as much as five units from the normal figures for the class of substance without, however, exhibiting complex anomaly, to justify a separate classification.

H. W.

### The Alcohols of the Hydroaromatic and Terpene Series.

III. *iso*Pulegol. ROBERT HOWSON PICKARD, HAROLD HUNTER, WILLIAM LEWCOCK, and HANNAH SMITH DE PENNINGTON (T., 1920, 117, 1248—1263).

1-Hydroxy-2-benzoylcamphor. A. L. W. E. VAN DER VEEN (*Zeitsch. Kryst. Min.*, 1920, 55, 627).—Colourless, sharply developed crystals 1 cm. across were crystallised from a warm solution in light petroleum. D 1.242; m. p. 95°. The symmetry-class is rhombic-bisphenoidal; as shown by the distribution of the faces and by etching;  $a:b:c=0.6535:1.0247:1$ . Optical data are given. Owing to the strong dispersion of the optic axes, brilliant colours are seen in parallel light between crossed nicols when viewed along an optic axis.

L. J. S.

Essential Oil of *Perylla nankinensis*, Dene. SEIJI FURUKAWA and ZENJIRO TOMIZAWA (*J. Chem. Ind. Tokyo*, 1920, 23, 342—363).—The formation, distribution, transformation, and chemical composition of the essential oil of *Perylla nankinensis*, Dene, were investigated. The oil and its parent substance (glucoside) are formed in the leaves only, but are later transported to the ear, and radiate from the sepals, the radiation being the most active during the flowering time. Both the oil and glucosides accumulate in the leaves gradually until the ears appear, and then remain constant until the beginning of the flowering time. With the appearance of the ears, the glucosides begin to decompose, finally disappearing after flowering. The oil distilled from the fresh plants at different stages of growth shows a gradual increase in aldehydes and decrease in ester until the end of the flowering time, whilst the oil from dried plants shows the reverse. The solubility of the oil decreases with the growth of the plants. To convert the glucosides into oil, the plants must be dried at low temperature to avoid decomposition of enzyme, which causes

resinification and decrease of solubility of the oil. The essential oils contain 20—30% of *l*-limonene, 44—57% of perillaldehyde, and a little  $\alpha$ -pinene. The various derivatives of perillaldehyde were prepared and their properties studied. Perillaldehyde has b. p.  $237^{\circ}$ ,  $D_{15}^{20}$  0.9675,  $[\alpha]_D^{20}$   $-145.8^{\circ}$ . The  $\alpha$ -anti-aldoxime of the aldehyde, colourless crystals, has m. p.  $102^{\circ}$ , and is exceedingly sweet, being two thousand times as sweet as sugar and four to eight times as sweet as saccharin. The hydrochloride of the oxime, unstable, white crystals, has m. p.  $114^{\circ}$ . The  $\beta$ -syn-aldoxime, colourless, triclinic prisms, has m. p.  $129^{\circ}$ , and is not sweet. The phenylhydrazone, silky needles, and semicarbazone, colourless crystals, have m. p.  $107.5^{\circ}$  and  $190$ — $199^{\circ}$  respectively. Perillonitrile,  $C_9H_{13}\cdot CN$ , has b. p.  $123^{\circ}/15$  mm. and  $D_{15}^{20}$  0.9488—0.9490, and is one-half as sweet as saccharin. Perillic acid, m. p.  $132$ — $133^{\circ}$ , yields an amide,  $C_9H_{13}\cdot CO\cdot NH_2$ , colourless crystals, m. p.  $164$ — $165^{\circ}$ . Perilla alcohol, b. p.  $118$ — $121^{\circ}/11$  mm.,  $D$  0.9690, forms an acetate, b. p.  $123$ — $124^{\circ}/13$  mm.,  $D$  0.9800.

## CHEMICAL ABSTRACTS.

***p*-Cymene as a Solvent.** A. S. WHEELER (*J. Amer. Chem. Soc.*, 1920, **42**, 1842—1846).—Spruce turpentine consists largely of *p*-cymene, and for the isolation of the latter, air at the ordinary temperature is first drawn through the turpentine for ten hours, and then the turpentine is distilled with superheated steam in an apparatus arranged so that the vapours pass first through a 30% solution of sodium hydroxide and then into the condenser. The distillate is purified by shaking it with a 5% solution of sodium hydroxide, and then distilling it over sodium. So prepared, *p*-cymene has b. p.  $176$ — $176.5^{\circ}$  and  $n_{D}^{12.5}$  1.4905.

The solubilities of a whole series of organic compounds in this solvent have been determined, and are tabulated. Pure *p*-cymene containing a trace of *p*-anisidine only slowly turns yellow when exposed to light, whereas an impure specimen turns red. W. G.

**The Acceleration of Vulcanisation. I.** D. F. TWISS and S. A. BRAZIER (*J. Soc. Chem. Ind.*, 1920, **39**, 125—132T).—The temperature-coefficient for the vulcanisation process has approximately the same value for a mixture of rubber and sulphur as for a similar mixture containing aldehyde-ammonia as catalyst. The progress of the reaction is illustrated by curves representing the rate of attainment of a maximum tensile strength, the gradual decrease in extensibility, and the increase in the proportion of sulphur in combination with the rubber. Results are quoted of experiments using other substances as catalysts, and it is shown that *m*-phenylenediamine is less active than *p*-phenylenediamine.

D. F. T.

**The Acceleration of Vulcanisation. II. A Discontinuity in the Effect of Vulcanisation.** D. F. TWISS and C. W. H. HOWSON (*J. Soc. Chem. Ind.*, 1920, **39**, 287—289T).—The effect of 1% of "light" magnesium oxide in accelerating



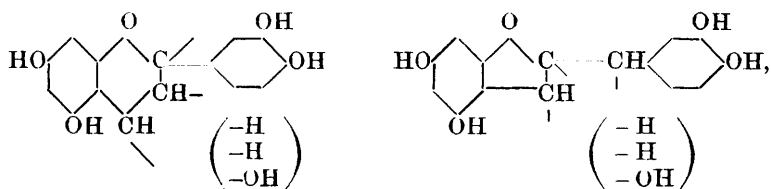
vulcanisation is approximately equal to that of 0.5% of potassium hydroxide introduced as a solution in glycerol. Mercuric oxide also exerts a distinct catalytic effect. When 1% of hexamethylene-tetramine is used as a catalyst in the presence of 1% of zinc oxide, the extensibility of the rubber does not decrease steadily, in the normal manner with progressive vulcanisation, but, after an initial decrease, suddenly begins to increase; after a brief period of this abnormal behaviour, a maximum is attained, and the rubber then resumes the normal decrease in extensibility.

D. F. T.

**Constitution of Catechin. II.** MAXIMILIAN NIERENSTEIN (T., 1920, 117, 1151—1156).

**Tannins. V. Phloroglucinol Tannins and Catechins. Constitution of Gambier Catechu.** KARL FREUDENBERG (*Ber.*, 1920, 53, [B], 1416—1427).—The author classifies as catechins a number of substances which contain two benzene nuclei, one of which is phloroglucinol, whilst the other varies, but is commonly catechol. They are distinguished from the flavone dyes and anthocyanidins by a higher hydrogen content. They are colourless, form colourless lead salts, and do not unite with mineral acids. They are sparingly soluble in cold, freely in hot, water. They give the pine-shaving reaction with phloroglucinol and yield characteristic azobenzene derivatives. Their most characteristic property is their ability, in the presence of ferments or mineral acids in hot aqueous solution, or even when dried, both in presence and absence of atmospheric oxygen, to condense to amorphous tannins, the simpler members of which are colourless and soluble in water, whilst the more complex derivatives are insoluble and more or less coloured. This classification includes, not only the three ordinary catechins, but also substances such as cyanomaclurin, aromadendrin, colatin, cacaole, and others. When, now, the catechins are grouped together as phloroglucinol tannins, their behaviour is found to vary from member to member in precisely the same manner as that of the nearly related flavone dyes, anthocyanidins, and phenyl styryl ketones, so that the whole series appears to be similarly constituted. It is therefore the more remarkable that the only catechin which has been closely investigated should have had a formula assigned to it (von Kostanecki, A., 1907, i, 73, 334; 1908, i, 86) widely different from that of the natural dyes mentioned above, since it is considered to be derived from an ethyldiphenylmethane, whilst the latter are derivatives of  $\alpha$ -diphenylpropane. By the action of sodium and alcohol on catechin tetramethyl ether, followed by further methylation, von Kostanecki has obtained a pentamethyl ether which he considered to be 2 : 4 : 6-trimethoxy-3-ethylphenyl-3' : 4'-dimethoxyphenylmethane, but which is now shown to be pentamethoxy- $\alpha$ -diphenylpropane. Von Kostanecki's formula for Gambier catechu is therefore abandoned in favour of one of the alternative formulæ,

of which the author inclines to the latter, since the colour reactions of the tetramethyl ether resemble those of the coumarans.



The preparation of veratraldehyde from protocatechualdehyde is fully described, as is also that of phloroglucinol trimethyl ether (the latter is conveniently obtained by preliminary treatment of phloroglucinol with methyl alcohol and hydrogen chloride, followed by complete methylation with methyl sulphate or by the action of heat on trimethylcarbonatophloroglucinol, b. p. 195—200°/Volmer pump vacuum). The phloroglucinol ether is converted into trimethylphloroacetophenone, which condenses with veratraldehyde to 2:4:6-trimethoxyphenyl 3':4'-dimethoxystyryl ketone (compare Tutin and Caton, T., 1910, **97**, 2062). On reduction with hydrogen in the presence of platinum, the unsaturated ketone is reduced to 2:4:6:3':4'-pentamethoxy- $\alpha\gamma$ -diphenylpropane, colourless, rectangular crystals, m. p. 87—88°, which is identical in all respects with the ether obtained from Gambier catechu by Kostanecki and Lampe (*loc. cit.*), for which, however, these authors found a somewhat lower melting point (compare Nierenstein, T., 1920, **117**, 971, 1151).

H. W.

**Lignin. III. Preparation of a Tannic Acid from the Lignosulphonic Acids.** MAX HÖNIG and WALTER FUCHS (*Monatsh.*, 1920, **41**, 215—222. Compare this vol., i, 291).—When aqueous solutions of the barium salts of the three fractions of the lignosulphonic acids are boiled with saturated barium hydroxide solution, they yield insoluble precipitates and readily soluble substances. The former differ from one another, and their composition has not yet been elucidated; they are all readily oxidised by alkaline permanganate, but the only product which could be characterised definitely was oxalic acid, obtained from the first fraction. The soluble substances, on the other hand, appear to be identical with one another, and the analytical results are in agreement with the formula  $C_{18}H_{30}O_{10}S\text{Ba}$ , so that they are probably derived from an acid,  $\text{OMe}\cdot C_{16}H_{22}O_4(\text{SO}_3\text{H})\cdot\text{CO}_2\text{H}$ . The aqueous solution of the salt gives greenish-grey, green, and white precipitates with iron chloride, copper chloride, and lead acetate respectively, and voluminous precipitates with quinine hydrochloride and gelatin; it is almost quantitatively precipitated by formaldehyde and hydrochloric acid. About 70% of it is absorbed

from acid solution by hide powder. The substance therefore has all the properties of a tannic acid of the catechu group, with such modifications as are caused by the sulphur content; when fused with potassium hydroxide, it gives protocatechuic acid in good yield. H. W.

**Thionaphthen in Coal Tar.** R. WEISSGERBER and O. KRUBER (*Ber.*, 1920, **53**, [B], 1551—1565).—The presence of thionaphthen in coal tar has frequently been suspected, particularly since its investigation by Gattermann and Lockhardt (*A.*, 1894, i, 92), and subsequently by Bezdrík, Friedländer, and Koeniger (*A.*, 1908, i, 200), has shown that it is extraordinarily like naphthalene, but up to the present all the efforts which have been made to identify it have been unsuccessful. This, however, has now been accomplished in the following manner, the method adopted being in the first instance similar to that used by V. Meyer for the isolation of thiophen. Crude naphthalene is sulphonated with a greatly deficient amount of sulphuric acid at 90—100°, and the sulphonated product is decomposed with steam in the presence of a little sulphuric acid at 145°. The product has m. p. about 73° and contains 2—3% of sulphur. Repetition of the process gives a material containing about 5—6% of sulphur, which can be increased to 12—14% by freezing out the naphthalene. The product obtained in this manner is dissolved in glacial acetic acid and treated with hydrogen peroxide, when thionaphthen-S-dioxide, long needles, m. p. 142°, is obtained, which is identical in all respects with the synthetic product. The actual isolation of thionaphthen from “enriched” naphthalene has been effected by the use of Friedländer’s mercuric acetate method (*loc. cit.*), but it is essential to guard against undue rise in temperature during the action, which can be readily effected by working with methyl-alcoholic solutions. By a similar process of partial sulphonation, followed by use of mercuric acetate, it has been found possible to isolate thionaphthen from technical “pure” naphthalene (containing 0.3—0.4% S), about 2 grams of the substance being obtained from 80 kilos. of naphthalene.

The industrial preparation of thionaphthen from crude naphthalene has also been investigated. It is found that thionaphthen is converted by sodium at 100—120° into a yellowish-brown sodium compound, which can readily be freed from adherent impurities by washing with benzene, and which decomposes, with re-formation of thionaphthen, when treated with ice-cold water; the yields, however, leave much to be desired, and the heating requires to be very carefully regulated. Far better results are obtained when sodamide is used (in the proportion of two molecules to one molecule of thionaphthen); reaction is complete at 120°, and practically the whole of the thionaphthen is liberated by water, the simultaneous formation of sodium sulphide appearing to be avoided. The process is applicable to “enriched”

naphthalene, and it is further found that the pre-formed sodamide may with advantage be replaced by sodium and dry ammonia.

The constitution of the sodium compound is discussed, but a definite conclusion is not reached. The possible desmotropic forms all contain a reactive methylene group, the presence of which cannot be established by the usual reagents, such as aromatic aldehydes, nitrous acid, or ethyl oxalate, which are indifferent towards thionaphthen. Under special conditions, however, the latter reacts with magnesium ethyl bromide, giving a compound, which is decomposed by carbon dioxide into thionaphthen-2-carboxylic acid, m. p. 236° (see later). At least one hydrogen atom must therefore be regarded as labile, and it must be assumed that the presence of the sulphur atom thus influences the neighbouring hydrogen atom, since substitution occurs preferably, and sometimes exclusively, in this position.

The action of carbon dioxide on sodium thionaphthen suspended in an indifferent solvent, such as toluene, gives rise to a mixture of the sodium salts of thionaphthen-2-carboxylic and -2:3-dicarboxylic acids, which can be separated by taking advantage of the widely differing acidities or by fractionation of their esters. The latter acid has been described previously, and the former is orientated by converting it through its azide into the well-known  $\alpha$ -hydroxythionaphthen. It appears that the product obtained by fusion with sodamide consists of about two-thirds monosodium- and one-third disodium-thionaphthen.

The following individual compounds are described: *methyl thionaphthen-2-carboxylate*, coarse prisms, m. p. 72—73°, b. p. 171°/14 mm.; *ethyl thionaphthen-2-carboxylate*, indistinct crystals, m. p. 36—37°, b. p. 181—183°/vacuum; *thionaphthen-2-carboxylic acid*, colourless, slender needles, m. p. 236° (*chloride*, colourless leaflets, m. p. 88—89°, b. p. 173—175°/19 mm.; *amide*, slender needles or leaflets, m. p. 177°; *hydrazide*, colourless, shining leaflets, m. p. 184—185°; *azide*, long, colourless needles, m. p. 108° [decomp.]); *urethane* of 2-aminothionaphthen, yellow crystals, m. p. 161°; 2-hydroxythionaphthen, m. p. 34—35° (the acid is not identical with that prepared by Friedländer and Link from *o*-mercaptobenzaldehyde and chloroacetic acid, which has m. p. 114°, and is designated thionaphthen-2-carboxylic acid by these authors); *methyl thionaphthen-2:3-dicarboxylate*, long, colourless prisms, m. p. 91°, b. p. 213—215°/18 mm.; thionaphthen-2:3-dicarboxylic acid, m. p. 250—251°; *thionaphthen-2:3-dicarboxylic anhydride*, pale yellow needles, m. p. 171°; *thionaphthen-2-carboxyamido-3-carboxylic acid*,  $C_6H_4 \begin{array}{c} \text{C}(\text{CO}_2\text{H}) \\ \text{S} \end{array} \text{C} \cdot \text{CO} \cdot \text{NH}_2$ , short, colourless needles, m. p. 221° (decomp.), and *thionaphthen-3-carboxyamido-2-carboxylic acid*,  $C_6H_4 \begin{array}{c} \text{C}(\text{CO} \cdot \text{NH}_2) \\ \text{S} \end{array} \text{C} \cdot \text{CO}_2\text{H}$ , short needles grouped in rosettes, m. p. 193° (decomp.), are obtained by the action of methyl-alcoholic ammonia on the

anhydride, and are separated by fractional crystallisation from glacial acetic acid. Their constitution is deduced by degrading them by Hofmann's method to the corresponding amino-acids, and warming the latter with dilute sulphuric acid, whereby they are converted into 2-hydroxythionaphthen, m. p. 34—35°, and 3-hydroxythionaphthen, m. p. 70°, respectively. *Thionaphthen-2:3-dicarboxylimide*, golden-yellow leaflets, m. p. 236—237°, is prepared by heating either of the acid amides at 200—220° until evolution of water vapour ceases, or, less advantageously, by heating the anhydride in a current of ammonia or by melting the anhydride with the calculated amount of carbamide. Degradation of the imide by Hofmann's method yields exclusively 3-hydroxythionaphthen, so that thionaphthen can readily be converted into thioindigo-red through thionaphthen-2:3-dicarboxylic acid.

H. W.

#### Additive Compound of Cinchonine and Cacodyl Chloride.

L. C. MAILLARD and E. MURLAY (*Bull. Soc. chim.*, 1920, [iv], 27, 756—769).—Cacodyl chloride combines directly or in chloroform solution with cinchonine to give a compound,  $C_{19}H_{22}ON_2, Me_2AsCl$ , and the crystals obtained from chloroform solution contain two molecules of the solvent. This compound is immediately decomposed by water, and cacodyl oxide is obtained. If the compound is decomposed by commercial ether, the anhydrous basic hydrochloride of cinchonine,  $C_{19}H_{22}ON_2, HCl$ , is obtained in a crystalline form. In the additive compound described above, the chlorine may be estimated directly by addition of nitric acid and silver nitrate.

W. G.

**Proteinogenous Amines. VI. The Preparation of Histidine from Blood Corpuscle Paste.** MILTON T. HANKE and KARL K. KOESSLER (*J. Biol. Chem.*, 1920, 43, 521—526).—The authors describe in full detail a process for the preparation of histidine from blood corpuscle paste; an average yield of 15 grams of pure histidine dichloride is obtained from 500 c.c. of the paste.

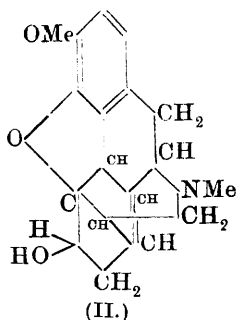
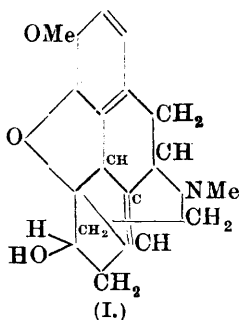
J. C. D.

**Preparation of Compounds of the Morphine Alkaloids with a Derivative of Barbituric Acid.** SOCIETY OF CHEMICAL INDUSTRY IN BASLE (D.R.-P. 322335; from *Chem. Zentr.*, 1920, iv, 392).—The alkaloids of the morphine group or their derivatives, either in the free state or as salts, are allowed to react with diallylbarbituric acid in the presence of a suitable solvent or diluent if required. The following compounds are described: *morphine-diallylbarbituric acid*, needles, m. p. 258°; *diacetylmorphine-diallylbarbituric acid*, colourless crystals, m. p. 186°; *ethylmorphine-diallylbarbituric acid*, crystalline mass; *allylmorphine sulphate*, m. p. 171°; *allylmorphine-diallylbarbituric acid*; *codeine-diallylbarbituric acid*, m. p. 105°; *dihydromorphine-*

*diallylbarbituric acid*, m. p. 125°; *dihydrocodeine-diallylbarbituric acid*, m. p. 95°.

H. W.

**Codeine.** MARTIN FREUND, W. W. MELBER, and ERICH SCHLESINGER (*J. pr. Chem.*, 1920, [ii], 101, 1—37).—During recent years, doubts have been cast on the validity of the formula



(I) proposed for codeine by Knorr and his co-workers, by Gadamer and von Braun (*A.*, 1914, i, 1138), and the alternative formula (II) has been put forward by Freund (compare Freund and Speyer *A.*, 1916, i, 738).

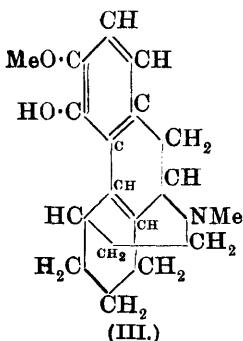
A series of attempts to gain further insight into the problem is now described; those starting from dihydrocodeine or chlorodihydrocodeine did not furnish the desired information, but better results were obtained with deoxycodine (Knorr and Waentig, *A.*, 1917, i, 957) as initial material. This substance is reduced by sodium and alcohol to a compound, which has been described by the latter authors as dihydrodeoxycodine, but which is now shown to be a tetrahydro-derivative; when, however, it is acted on by palladium and hydrogen, an isomeric tetrahydro-derivative is produced, the formation of which cannot be accounted for on the basis of Knorr's formula, but which is readily explained by the authors' modification thereof.

Dihydrocodeine, m. p. 86—88° (Oldenburg, D.R.-P. 260233, gives 62—63°), is unaffected by treatment with sulphuric and chromic acids under varied conditions, but is transformed by concentrated nitric acid in glacial acetic acid solution into *nitrodihydrocodeine*, yellow, crystalline powder, m. p. 221°. *Dihydrocodeine methiodide*, m. p. 257°, is readily obtained from its components, and is converted by dilute potassium hydroxide solution into *de-N-methyldihydrocodeine*, which could not be caused to crystallise, but which was readily converted into *de-N-methyldihydrocodeine methiodide*, colourless leaflets ( $+ \frac{1}{3} \text{H}_2\text{O}$ ), m. p. 173—176° (decomp.) after softening at 170° (the *perchlorate* of the base has m. p. 201—202°). *Dihydrode-N-methyldihydrocodeine* is obtained as a pale yellow, non-crystallisable syrup by the reduction of *de-N-methyldihydrocodeine* by hydrogen in the presence of palladium, and yields a *methiodide*, yellow powder, m. p. 219—221°, from alcohol or glacial acetic acid, colourless rods, m. p. 221—224°, from water. The methiodides evolve trimethylamine abundantly when treated with concentrated alkali hydroxide,

but the corresponding nitrogen-free bases are too readily decomposed to permit their isolation.

In the hope of obtaining better results with an analogous substance in which the hydroxyl group is not present, dihydrocodeine has been converted by phosphorus pentachloride in chloroform solution into *chlorodihydrocodide*, plates, m. p. 172—174°, which is transformed by hydrogen peroxide into *chlorodihydrocodide amino-oxide*, colourless leaflets (+3H<sub>2</sub>O), m. p. 214° (decomp.), which yields the original material on treatment with sulphurous acid, and by nitric acid in hot glacial acetic acid solution is converted into a substance, C<sub>21</sub>H<sub>24</sub>O<sub>5</sub>N<sub>2</sub>Cl [?], pale yellow, crystalline powder, m. p. 223—224°, the constitution of which was not further elucidated. *Chlorodihydrocodide methiodide*, small, colourless, matted needles, m. p. 244° (decomp.), is prepared from its components, and is converted by potassium hydroxide into *de-N-methylchlorodihydrocodide*, m. p. 103° after previous softening, which combines with methyl iodide to give *de-N-methylchlorodihydrocodide methiodide*, colourless needles, m. p. 272°; the corresponding nitrogen-free base was too unstable to permit its isolation. *De-N-methylchlorodihydrocodide* is reduced by hydrogen in the presence of palladium to *dihydrode-N-methylchlorodihydrocodide*, which could not be caused to crystallise, but which readily yields *dihydrode-N-methylchlorodihydrocodide methiodide*, colourless, slender needles decomposing at 290—291°; the latter is decomposed by boiling alkali, with evolution of trimethylamine and simultaneous decomposition of the nitrogen-free substance.

$\alpha$ -Chlorocodide is reduced by hydrogen in the presence of colloidal palladium to  $\alpha$ -*dihydrodeoxycodine*, which could not be caused to crystallise; it yields an oily *hydriodide*, *methiodide* and *perchlorate*, and a solid, but amorphous, *picrate*; *aurichloride*, and *platinichloride*.

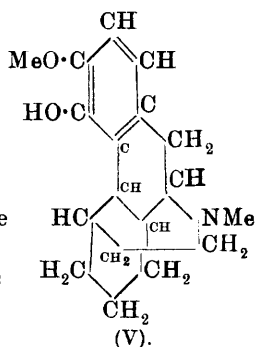
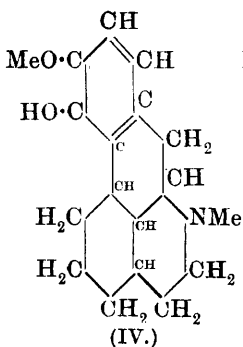


*Dihydrodeoxycodine* (III), coarse, crystalline plates (+0.5H<sub>2</sub>O), m. p. 117—119°, [ $\alpha$ ]<sub>D</sub><sup>18</sup> + 88.71° in alcoholic solution (*hydriodide*, pale brown needles, m. p. 245°), is prepared by the electrolytic reduction of chlorodihydrocodide at a lead cathode, or in a similar manner from  $\alpha$ - or  $\beta$ -chlorocodide or from deoxycodine; the base obtained from  $\beta$ -chlorocodide, however, had m. p. about 126—130° after previous softening. The

phenolic character of the base derived from deoxycodine is particularly established by the isolation of the *methiodide* of the *methylated base*, long, flat needles, m. p. 245°. It would appear that deoxycodine is not formed, as Knorr and Waentig (*loc. cit.*) suggest, by simple replacement of the hydroxyl group by hydrogen, but that it is formed by fission of the oxygen bridge.

Deoxycodine hydrochloride is obtained by a modification of the

method of Knorr and Waentig (*loc. cit.*), and is reduced by



hydrogen in aqueous solution in the presence of palladium to  $\beta$ -tetrahydrodeoxycodeine (IV); the base crystallises from methyl or ethyl alcohol in six-sided leaflets (+ 1 molecule of solvent), m. p. 147—148°; it is feebly laevorotatory in alcoholic solution. The hydrochloride, m. p.

about 262° (+1EtOH), the hydriodide, long needles (+H<sub>2</sub>O), m. p. 240—241°, and the methiodide, m. p. 263°, are described. All attempts to hydrogenate the base further were unsuccessful. The *N*-methyl group could not be removed by means of cyanogen bromide. The presence of the hydroxyl group could not be established by the help of acetic anhydride, benzoyl chloride, or chloroacetyl chloride, but the base is converted by methyl sulphate and sodium hydroxide into methoxytetrahydrodeoxycodeine, which was identified as the methiodide, prisms, m. p. 255—256° after previous softening; the latter is converted by very concentrated potassium hydroxide solution into *de-N*-methylmethoxytetrahydrodeoxycodeine, pale yellow oil, which yields a hydriodide, small rods, m. p. about 185° after softening from 175°, and a methiodide, prismatic rods, m. p. 188° after softening at 185°. The action of concentrated potassium hydroxide solution on the methiodide leads to the copious evolution of trimethylamine and the formation of small quantities of a pale yellow oil, which could not be caused to crystallise. Bromotetrahydrodeoxycodeine,



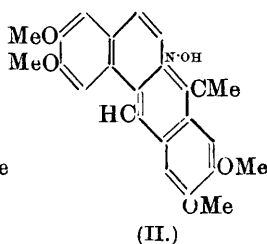
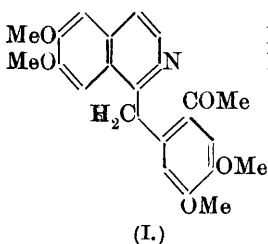
needles, m. p. about 135° (decomp.) after softening from 120°, is prepared by the interaction of bromine and the  $\beta$ -base in chloroform solution; the hydrochloride, hydrobromide, and hydriodide are viscous salts, which could not be caused to crystallise. When subjected to electrolytic reduction, the bromo-compound regenerates the parent substance.  $\alpha$ -Tetrahydrodeoxycodeine (formula V), small leaflets or rods, m. p. 132°, is prepared by the reduction of dihydrodeoxycodeine, m. p. 117—119°, by hydrogen and palladium, or by electrolytic reduction of  $\alpha$ -dihydrodeoxycodeine. The identity of this substance with the "deoxydihydrocodeine" obtained by Knorr and Waentig by the action of sodium and alcohol on deoxycodeine is established by its melting point and that of its hydrochloride [155° (decomp.)], and also by its conversion into  $\alpha$ -methoxytetrahydrodeoxycodeine methiodide, m. p. 247° (Knorr and Waentig give m. p. 248—249°).

H. W.



**Acetylpapaverine and Coralyne [Hexadehydrocoralydine].**

WILHELM SCHNEIDER and KURT SCHROETER (*Ber.*, 1920, **53**, [B], 1459—1469).—Papaverine is converted by acetic anhydride, which has been previously warmed to 85° with a little concentrated sulphuric acid, into a yellow, crystalline salt,  $C_{24}H_{25}O_9NS, H_2O$ . The corresponding quaternary ammonium base passes in warm aqueous solution into an isomeric ketonic base, from which the original salts are regenerated by addition of acid. The phenomena are thus very similar to those observed with berberine, and, more particularly, with dehydrocorydaline (Haars, A., 1905, i, 462), from which the present compound differs in containing two atoms of hydrogen less in the molecule. The constitution of the substance is further elucidated by its conversion into *m*-hemipinic acid; it behaves in this respect in the same manner as coralydine (Pictet, A., 1913, i, 1224; 1916, i, 418), and for this reason the



authors propose the name coralyne. It therefore appears that the primary product of the action of sulphoacetic anhydride on papaverine is acetylpapaverine (I), which passes by ring closure into

the sulphoacetate of the isomeric quaternary coralyne base (II).

*Coralynesulphoacetate*,  $C_{22}H_{22}O_4N \cdot SO_3 \cdot CH_2 \cdot CO_2H, H_2O$ , forms intensely yellow needles, m. p. 277° (decomp.), which fluoresce strongly in aqueous solution. The following salts are readily prepared from it: *chloride*,  $C_{22}H_{22}O_4NCl, 2.5H_2O$ , slender, yellow needles; *iodide*,  $+ H_2O$ , golden-yellow needles, m. p. 278° (decomp.); *hydrogen sulphate*,  $+ 2.5H_2O$ , voluminous, pale yellow precipitate; *nitrate*,  $+ H_2O$ , small, yellow needles, which decompose above 270° without appearing to melt.

*Acetylpapaverine* ( $\psi$ -coralyne), yellowish-grey crystals, m. p. 140—141°, is readily obtained by heating a solution of coralydyl sulphoacetate in water with an excess of sodium hydroxide until the solution, which originally has a dark colour, owing to the presence of the ammonium hydroxide form of coralyne, becomes pale orange; the  $\psi$ -base is stable in the dry state or when dissolved in benzene, but on contact with water or alcoholic solutions is more or less rapidly converted into the ammonium form, the rate being generally such as can be readily followed by titration with *N*/10-acid. It is interesting to note that this change is accompanied by the development of fluorescence in the solution. *Acetylpapaverineoxime* has m. p. 207°, whilst the *phenylhydrazone* forms colourless, matted needles, m. p. 208°. When treated with methyl iodide in benzene solution at 100°, acetylpapaverine gives the corresponding *methiodide*, small, pale yellow needles,

m. p. 219—220°, but in methyl-alcoholic solution it yields the quaternary coralyne iodide.  
H. W.

**Esterification of Unsymmetrical Di- and Poly-basic Acids. XXXIV. Affinity Constants and Esterification of the Pyridinecarboxylic Acids.** RUDOLF WEGSCHEIDER (*Monatsh.*, 1920, **41**, 185—198).—It has been shown (this vol., i, 740) that the formation of hydrogen esters of aminodicarboxylic acids takes place, generally, in a fairly regular manner, except in the instance of the semi-hydrolysis of the normal esters, and attempts are now made to secure a more uniform conception of the esterification of the pyridinecarboxylic acids than has previously been possible. It is found that the apparently irregular affinity constants of the pyridinecarboxylic acids can be brought into line with the Ostwald factor rule in the same manner as the aromatic acids if it is assumed that these constants are influenced by internal salt formation. In general, the same factors can be used for the substituents as in the case of the aromatic acids, except for the methyl group, for which larger factors must be chosen. The formation of hydrogen esters of the pyridinecarboxylic acids in general follows the same rules as are usually valid if a steric influence is not ascribed to the nitrogen atom of the ring, and the strength of the carboxyl group is regarded as determined by a suitably modified factor rule. Exceptions are only encountered in the case of semi-hydrolysis, and this is by no means unusual.

H. W.

**Manufacture of the Allyl Ester of 2-Phenylquinoline-4-carboxylic Acid.** SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat., 150401).—Like the alkyl esters, the allyl ester of 2-phenylquinoline-4-carboxylic acid is tasteless, and has the further advantage of dissolving uric acid more readily than either the alkyl esters or the acid itself. It may be prepared by any of the usual methods of esterification, such as the action of an allyl haloid on a salt of the acid or by the action of allyl alcohol on the acid chloride, or on the acid itself in presence of hydrogen chloride or sulphuric acid. The ester boils at 260°/15 mm., and melts at 30°. Its hydrochloride crystallises from alcohol in small, citron-yellow needles, m. p. 145—147°, which are immediately decomposed by water.

G. F. M.

**Quinuclidines.** JAKOB MEISENHEIMER (*Annalen*, 1920, **420**, 190—239).—The term quinuclidines has been ascribed by Koenigs (A., 1905, i, 824) to a series of bases derived from piperidine by joining the nitrogen atom to the para-carbon atom by a bridge of two carbon atoms, and the isolation of 3-ethylquinuclidine has been described. The present communication deals with the preparation of quinuclidine itself and of benzoquinuclidine according to the general method of Koenigs. The former substance has been described previously by Löffler and Stietzel (A., 1909, i, 181), but

their data differ so widely from those of the present author that it is impossible for them to have been dealing with the pure compounds. (In the following, their data are recorded in brackets after the individual substances.)

[With JULIUS NERESHEIMER and WILHELM SCHNEIDER.]—4-Pyridylethanol, colourless, viscous syrup, b. p. 151—152°/13—14 mm. (125—126°/15 mm.), is prepared by the action of formaldehyde on 4-methylpyridine, obtained by fractionation of commercial 3-methylpyridine [the method of purification by means of mercuric chloride recommended by Ahrens (A., 1905, i, 232) does not appear to be effective]; the yield is only very small, owing to the simultaneous production of di- and tri-methylol. The corresponding picrate has m. p. 134—135° (122—123°). The alcohol is converted by fuming hydriodic acid and red phosphorus into 4-pyridylethyl iodide hydriodide, m. p. 186—187° after darkening at about 180°, from which the corresponding picrate, slender, pale yellow needles, m. p. 114—115° (108—110°), is obtained; the latter readily decomposes in boiling aqueous or alcoholic solution, with the formation of 4-vinylpyridine picrate (see later). 4-Pyridylethyl iodide is a colourless oil, which readily decomposes spontaneously into a polymeric iodide, m. p. 267—268° (decomp.) after softening at 260° (216—218°). 4-Pyridylethyl chloride hydrochloride, m. p. above 260° (decomp.), is prepared from 4-pyridylethanol and fuming hydrochloric acid; the corresponding picrate crystallises in slender, yellow needles, m. p. 130—131°, whilst the platinichloride has m. p. 207° (decomp.) (147—148°). The free base is a colourless oil, which readily loses hydrogen chloride and forms 4-vinylpyridine in the presence of alkali hydroxide; it is transformed when gently warmed into a polymeric quinuclidine chloride, m. p. 255—260° (decomp.).

4-Vinylpyridine, almost colourless oil, b. p. 59°/12 mm. (slight decomp.), is best obtained by the action of boiling methyl-alcoholic potassium hydroxide solution on 4-pyridylethyl iodide hydriodide [the picrate, yellow, shining leaflets, m. p. 198—199° (decomp.) after previous softening when slowly heated, and the platinichloride, which softens at about 200°, but does not melt below 350°, are described]. Potassium permanganate oxidises it to a mixture of formic and isonicotinic acids.

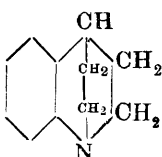
4-Piperidylethanol, almost colourless, viscous liquid, b. p. 140—141°/12—14 mm. (120—125°/15 mm.), is prepared by the reduction of 4-pyridylethanol by sodium and ethyl alcohol, and is converted by fuming hydriodic acid and red phosphorus into 4-piperidylethyl iodide hydriodide, colourless needles, m. p. 190—191° after darkening at 186° (158—159°). The latter is transformed by a slight excess of sodium hydroxide in warm aqueous solution into quinuclidine, which is conveniently isolated as the picrate, m. p. 275—276° (decomp.) after previous softening (213—215°); the free base has m. p. 158° after softening at 154° in a sealed capillary tube, and is very volatile for a substance of such high melting point. It is remarkably stable, and is scarcely

affected by concentrated sulphuric acid or nitric acid at  $100^{\circ}$ , or by potassium permanganate in sulphuric acid solution. The *platinichloride*, m. p.  $238-240^{\circ}$  (decomp.), and the *aurichloride*, large, shining leaflets, m. p.  $271-273^{\circ}$  (decomp.) after previous softening, are described. Quinuclidine unites with ethyl iodide to give the corresponding *ethiodide*, thin plates, m. p.  $270-271^{\circ}$  (slight decomp.), from which the *platinichloride*, leaflets, m. p.  $271-272^{\circ}$  after previous darkening ( $212^{\circ}$ ), is obtained.

[With OSCAR FINN and WILHELM SCHNEIDER.]—Lepidine, when heated on the boiling-water bath with 20% formaldehyde solution, yields a mixture of 4-quinolylpropanediol (*picrate*, m. p.  $170^{\circ}$ ) and 4-quinolyethanol, prisms, m. p.  $63^{\circ}$  (*picrate*, m. p.  $155-157^{\circ}$ ) (compare Koenigs, *loc. cit.*). The ethanol is somewhat unstable towards hydrochloric acid, which, at  $100^{\circ}$ , converts it into the dimolecular 4-vinylquinoline (see later). It is converted by hydriodic acid (D 1.96) and red phosphorus at  $95^{\circ}$  into 4-*quinolylethyl iodide hydriodide*, yellow, six-sided plates, m. p.  $173^{\circ}$ ; the salt is stable towards light and air when pure, but loses hydrogen iodide when its aqueous or alcoholic solution is boiled, and forms dimolecular 4-vinylquinoline. 4-*Quinolylethyl iodide picrate* forms long needles, m. p.  $154^{\circ}$ . The corresponding free base is less stable than its salts, and loses hydrogen iodide in aqueous solution, with the formation of 4-vinylquinoline and other products. The readiest method of preparing 4-*vinylquinoline* consists in boiling a solution of 4-quinolylethyl iodide hydriodide in aqueous acetone with aqueous sodium hydroxide solution; the free base is purified through the *picrate*, slender needles, m. p.  $188-189^{\circ}$ , and is thus obtained as a pale brown, viscous oil, which gradually solidifies when preserved in a desiccator, and cannot be distilled even under greatly diminished pressure, owing to the readiness with which it polymerises. It is oxidised by potassium permanganate in sulphuric acid solution to formic and 4-quinolinecarboxylic acids. The *platinichloride*, broad needles, m. p. above  $275^{\circ}$ , is described. *Bimolecular 4-vinylquinoline*, coarse crystals, m. p.  $148-149^{\circ}$ , is obtained in the pure state by evaporation of a solution of the unimolecular variety in aqueous hydrochloric acid and cautious liberation of the base by addition of alkali in the presence of ether. It is neutral towards litmus, non-volatile with steam, and cannot be distilled; it does not decolorise acid permanganate. The *hydrochloride*, m. p. between  $280^{\circ}$  and  $290^{\circ}$ , the *platinichloride*, which does not melt below  $340^{\circ}$ , and the *picrate*, thin, yellow needles, m. p.  $242-243^{\circ}$  (decomp.) after previous softening and darkening, are described. 4-Vinylquinoline *picrate* is transformed by boiling absolute alcohol into 4-*quinolylethyl ethyl ether picrate*, broad, shining needles, m. p.  $171-172^{\circ}$  (decomp.) after marked softening at  $140^{\circ}$  when slowly heated, m. p.  $140-145^{\circ}$ , followed by resolidification and re-melting at  $171-172^{\circ}$ , when rapidly heated, the variations being due to the elimination of ethyl alcohol and formation of 4-vinylquinoline *picrate*, which then undergoes partial decomposition; a similar change appears to be caused by

boiling methyl alcohol, the *picrate* so obtained having m. p. 167—168° (decomp.). 4-*Quinolylethyl ethyl ether* is an almost colourless liquid, b. p. 169—170°/11—12 mm. [*platinichloride*, flat, golden-yellow prisms, m. p. 183—184° (decomp.) when rapidly heated].

*Tetrahydro-4-quinolylethanol*, pale yellowish-green, viscous liquid, b. p. 196—198°/11—12 mm., is prepared by the reduction of 4-quinolylethanol by sodium and ethyl alcohol; it does not yield a crystalline *picrate* or *platinichloride*, and reduces gold chloride to metallic gold. On treatment with red phosphorus and fuming



hydriodic acid, the ethanol gives *tetrahydro-4-quinolylethyl iodide hydriodide* (m. p. about 100—105° in the crude condition), which is converted by aqueous sodium hydroxide solution at 60—70° into *benzoquinuclidine* (annexed formula), shining leaflets, m. p. 68—69° (*platinichloride*, yellowish-red prisms, which soften at 225° and decompose at 230°; *picrate*,

slender needles, m. p. 195—196°). *Benzoquinuclidine ethiodide* forms long needles, m. p. 217—218°, and is converted by moist silver oxide into the corresponding quaternary base. H. W.

**Alkylation of Pyrazolones by means of Sodium Alkylloxides.** LUDWIG WOLFF and ERNST THIELEPAPE (*Annalen*, 1920, **420**, 275—284).—Wolff's method for the replacement of the oxygen atom of ketones and aldehydes by hydrogen which depends on the action of sodium ethoxide on the corresponding hydrazones (A., 1912, i, 988) gives partly abnormal results when applied to pyrazolones, since alkylation is found to occur.

When 3-methylpyrazolone is heated with methyl-alcoholic sodium methoxide for fifteen hours at 220° and subsequently for nine hours at 250° it yields a mixture of butyric acid (41%) and 3:4-dimethylpyrazolone (39%), colourless crystals, m. p. 267—268°, the identity of which is established by comparison with a specimen prepared from ethyl methylacetoacetate and hydrazine hydrate; with sodium ethoxide, 3-methyl-4-ethylpyrazolone, m. p. 229°, is mainly produced, butyric acid being formed in minor quantity, whilst, with sodium propoxide, 3-methyl-4-propylpyrazolone, m. p. 206—207°, is obtained. The success of the experiment is largely dependent on the use of absolutely anhydrous alcohol, since under similar conditions, but with Kahlbaum's propyl alcohol which had not been specially treated, pyrazolylpyrazolone, m. p. 259°, was isolated in good yield. 3:4-Dimethylpyrazolone was not affected by being heated with sodium ethoxide solution during twenty-two hours at 260°. Phenylmethylpyrazolone is transformed by sodium ethoxide at 170—190° into a mixture of bisphenylmethylpyrazolone, which does not melt below 300°, and bisphenylmethylethylpyrazolone, m. p. 149—150°; more complete ethylation is effected at 220°.

3:5-Dimethylpyrazole is converted by sodium ethoxide at 250°

into a substance,  $C_{12}H_{20}N_4$ , m. p.  $253^\circ$  [*picrate*, m. p.  $224-226^\circ$  (decomp.)], which is probably tetramethylethylpyrazolylpyrazole.

H. W.

#### New Cases of Isomerism in the Isatin Series. IV.

GUSTAV HELLER (*Ber.*, 1920, **53**, [B], 1545—1551. Compare A., 1917, i, 219).—Further experiments have shown that isatol has about three times the molecular weight calculated for the simple formula when dissolved in boiling glacial acetic acid or in freezing phenol or veratrole; the phenomenon is considered to be due to association rather than to polymerisation. The conversion of isatol into isatin is not a simple rearrangement, but appears to occur with intermediate formation of bimolecular isatoid-like substances. The typical properties of the isatols appear to be more clearly exhibited by dimethylisatol (the dimethylisatin, III, of A., 1918, i, 235), which is not immediately affected by alkali and is unimolecular as shown by the smooth conversion of its methyl ether into the unimolecular lactim ether when heated with glacial acetic acid; its ready conversion into a basic substance, insoluble in alkali, appears to differentiate it from methylisatoid.

The formula previously proposed for isatinone (A., 1919, i, 282) is now abandoned, since the substance is found to be identical with methylisatoid prepared by Baeyer and Oekonomides (A., 1883, 201); the name isatinol should therefore be deleted from the literature and replaced by *isomethylisatoid*. Various formulæ for these substances are considered, but a definite conclusion does not yet seem possible.

[With MARIE MEYER.]—5-Chloroisatol, m. p.  $188^\circ$  (decomp.), is prepared by converting chloroisatin into the silver salt and treatment of the latter with benzoyl chloride in the presence of benzene; it does not react with phenylhydrazine or with methyl sulphate at  $100^\circ$ , is not basic, and is converted by hot alkali into chloroisatinic acid. 5-Chloroisatin- $\alpha$ (2)-phenylhydrazone, slender needles, m. p.  $250^\circ$  (decomp.), is prepared from phenylhydrazine and chloroisatin lactim ether, m. p. about  $132^\circ$ , after softening at  $128^\circ$  in alcoholic solution; the lactim ether yields chloromethylisatoid when subjected to illumination or heated with glacial acetic acid. 5-Bromoisatol is prepared in the same manner as the corresponding chloro-compound. The silver salt of 5-bromoisatin is primarily converted by methyl iodide in benzene solution at  $100^\circ$  into 5-bromoisatin lactim ether, which is subsequently partly transformed into 5-bromo-N-methylisatin, needles, m. p.  $172-173^\circ$  (more conveniently prepared by the action of alcoholic sodium methoxide on 5-bromoisatin), the conversion appearing to occur more readily than with the corresponding parent substances. 5-Bromoisatin-2-phenylhydrazone forms dark red, four-sided platelets, which decompose at  $241-242^\circ$ .

H. W.

#### Azopyrazolones and Allied Compounds.

KENNETH HERBERT SAUNDERS (T., 1920, **117**, 1264—1272).

**Substituted Quaternary Azonium Compounds containing an Asymmetric Nitrogen Atom. III. Resolution of Phenylmethylethylazonium, Phenylbenzylpropylazonium, and Phenylbenzylallylazonium Iodides into Optically Active Components.** BAWA KARTAR SINGH (T., 1920, 117, 1202—1214).

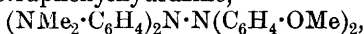
**Hydrazones and Azines. I. Coloured Ketazines.** OTTO GERHARDT (*Monatsh.*, 1920, 41, 199—214).—A number of ketazines have been prepared in the hope of tracing some connexion between colour and constitution in this class of substances. Even among the fluorenoneketazines, however, there seems to be no marked regularity; in spite of the presence of the chromophoric grouping,  $:C:N-$ , the close arrangement of the atoms in the molecule and the occurrence of crossed double bonds, the entrance of the auxochromic hydroxy-group in the meta-position causes only an unimportant deepening of the colour, but apparently no development of tinctorial power.

*$\beta$ -Hydrindoneketazine*, pale pink needles, m. p. 194—195°, which undergo autoxidation on exposure to air, yielding dark red needles which could not be fully identified, is prepared by the action of hydrazine hydrate on an alcoholic solution of  *$\beta$ -hydrindone*. *2-Nitrofluorenonehydrazone* forms dark yellow, microscopic leaflets, m. p. 214°, and is oxidised by iodine in alcoholic solution to *2-nitrofluorenoneketazine*, brown, crystalline powder, m. p. 305—306°. *2-Aminofluorenonehydrazone*, orange-yellow, matted needles, m. p. 201—202°, is prepared from 2-aminofluorenone and hydrazine hydrate; it cannot be oxidised by iodine to the corresponding ketazine, nor can the latter be obtained from it by the action of a further molecule of the ketone. *2-Acetylaminofluorenone*, cinnabar-red crystals, m. p. 227—228°, is, however, readily convertible into *2-acetylaminofluorenonehydrazone*, lemon-yellow leaflets, m. p. 212—214°, which, when treated with iodine, gives *2-acetylaminofluorenoneketazine*, brown, crystalline powder, m. p. 303—306°; attempts to remove the acetyl groups from the latter were unsuccessful, since 2*N*-alcoholic potassium hydroxide solution was without action, whilst a saturated solution converted the substance into a viscous mass. *2-Dimethylaminofluorenone*, dark red, crystalline powder, m. p. 146—147°, is prepared in 40% yield by the action of methyl sulphate on the aminoketone at 170—180°, and is so extensively resinified by the action of hydrazine hydrate that the corresponding hydrazone could not be isolated. *2-Hydroxyfluorenonehydrazone*, chrome-yellow, matted needles, has m. p. 201—202°, whilst the corresponding *ketazine*, m. p. 301—303°, is a brown, crystalline powder. *Piperonaldazine*, m. p. 206—207°, crystallises in pale yellow leaflets. *Benzophenone-benzil-ketazine*,  $CPh_2:N:N:CPh \cdot CPh$ , pale yellow crystals, m. p. 128—129°, is prepared from benzophenonehydrazone and benzil in the presence of a little alcohol at 150°, whilst *tetramethyldiaminobenzophenone-benzil-ketazine* forms orange-yellow leaflets, m. p. 173—174°.

H. W.

**Ditertiary Hydrazines. XXII. Basic Tetra-arylhydrazines.**

HEINRICH WIELAND (*Ber.*, 1920, **53**, [B], 1313—1328. Compare A., 1915, i, 848, and previous abstracts).—The preparation of further substituted tetra-arylhydrazines has been attempted; the most noteworthy of the substances actually isolated is *pp'*-tetramethyldiaminodimethoxytetraphenylhydrazine,



in which the tendency towards dissociation is as marked as in the case of tetra-*p*-dimethylaminotetraphenylhydrazine.

[With J. SUREDA.]—*pp'*-*Diacetylaminotetraphenylhydrazine*,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{NPh} \cdot \text{NPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}$ , colourless prisms, m. p.  $124^\circ$ , after slight decomposition from  $100^\circ$ , is obtained by the oxidation of *p*-acetylaminodiphenylamine by potassium permanganate in acetone solution; as is to be expected, the substance does not exhibit a strongly marked tendency towards dissociation, in which respect it resembles tetratolylhydrazine. Attempts to remove the acetyl groups without extensively decomposing the compound were unsuccessful.

[With E. SCHAMBERG.]—*p*-*Diethylaminodiphenylamine*, colourless leaflets, m. p.  $88$ – $89^\circ$ , is obtained by the action of phenylhydrazine on *p*-nitrosodiethylaniline, and is converted by silver oxide in dry ethereal solution into *di-p*-*diethylaminotetraphenylhydrazine*,  $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NPh} \cdot \text{NPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NEt}_2$ , m. p.  $104^\circ$  (darkening); in its tendency towards dissociation, the latter substance closely resembles tetra-anisylhydrazine. It is hydrolysed by water to diethylaminodiphenylamine, quinoneanil, and diethylamine. In benzene solution it readily unites with nitric oxide and triphenylmethyl to yield the compounds,  $\text{C}_{16}\text{H}_{19}\text{ON}_3$ , yellow needles, m. p.  $78^\circ$ , and  $\text{C}_{35}\text{H}_{34}\text{N}_2$ , coarse, colourless prisms, m. p.  $163^\circ$  (darkening), respectively.

[With FRL. E. HAAS.]—*p'*-*Dimethylamino-p*-methoxydiphenylamine, colourless leaflets, m. p.  $78^\circ$ , b. p.  $200^\circ/\text{ca. } 1 \text{ mm.}$ , is prepared by the action of *p*-iodoanisole, acetyldimethyl-*p*-phenylenediamine, potassium carbonate, copper bronze, and iodine in boiling nitrobenzene and subsequent hydrolysis of the primary product. When dissolved in a mixture of dry pyridine and ether and cooled in a freezing mixture of ice and salt, it is oxidised by silver oxide to *pp'*-tetramethyldiaminodimethoxytetraphenylhydrazine, quadratic prisms, m. p.  $93^\circ$ , after previous discoloration. Its solution in benzene readily absorbs nitric oxide with the formation of *p'*-dimethylamino-*p*-methoxydiphenylnitrosoamine, dark yellow leaflets, m. p.  $95^\circ$ .

[With E. SCHAMBERG.]—*Di-pp'*-*diethylaminodiphenylamine*, m. p.  $56^\circ$ , is prepared by reducing *p*-nitrosodiethylaniline with zinc dust, adding diethylaniline, oxidising with potassium dichromate, and reduction of the zinc double salt thus produced by hyposulphite. It differs from the corresponding tetramethyl base in that, as a consequence of extensive decomposition, it cannot be oxidised to the corresponding hydrazine; treatment with silver oxide in the presence of light petroleum transforms it into *diethylindophenol*, m. p.  $106^\circ$ .



Attempts to convert 2:4:6:2':4':6'-hexamethoxydiphenylamine into the corresponding hydrazine were unsuccessful. The substance is oxidised by silver oxide in acetone solution to *pentamethoxyquinoneanil*,  $\text{O}:\text{C}_6\text{H}_2(\text{OMe})_2:\text{N}\cdot\text{C}_6\text{H}_2(\text{OMe})_3$ , blackish-green, shining crystals, m. p.  $202^\circ$ , which is reduced by zinc dust and acetic acid to the corresponding *leuco-compound*, colourless needles, m. p.  $156\text{--}157^\circ$  (discoloration).

The oxidation of tetramethyldiaminodiphenylamine by an excess of silver oxide has been further studied, and the view taken previously that trimethylindamine [dimethylaminophenylmethylquinonedi-imide],  $\text{NMe}:\text{C}_6\text{H}_4:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , is produced by the loss of hydrogen and methyl from the base is now abandoned, since it is found that the solution which has only been oxidised to the hydrazine stage contains only traces of the indamine. The latter owes its origin to the oxidation of the tetramethyldiaminodiphenyl-nitrogen radicle,

$\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2 \rightarrow \text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{C}_6\text{H}_4:\text{NMe} + \text{CH}_3$ , but the fate of the methyl radicle is not established. Isolation of trimethylindamine is most conveniently effected by treatment of the fully oxidised ethereal solution of tetramethyldiaminodiphenylamine with nitric oxide and separation of the *trimethylindamine-dinitrosoamine*, yellowish-green crystals, m. p.  $136^\circ$  (decomp.) after softening at  $130^\circ$ . The latter is reduced by stannous chloride and concentrated hydrochloric acid to *trimethyldiaminodiphenylamine*, colourless needles, m. p.  $73^\circ$ , which is oxidised by silver oxide in the presence of ether to *trimethylindamine*, m. p.  $90^\circ$ ; nitric oxide and triphenylmethyl are readily added by the latter. H. W.

**Ditertiary Hydrazines. XXIII. Mixed Aromatic Ditertiary Hydrazines. Tetrabenzylhydrazine.** HEINRICH WIELAND and EDUARD SCHAMBERG (*Ber.*, 1920, **53**, [B], 1329—1335).—In continuation of previous work, the authors have now examined unsymmetrical diaryldialkylhydrazines, which, in regard to their tendency towards dissociation, are found to be even more stable than the corresponding symmetrical compounds. Attempts to prepare tetra-alkylhydrazines did not meet with success, but it has been found possible to isolate tetrabenzylhydrazine, which is found to possess extraordinary stability. It appears, therefore, that the instability of the N·N linking in hydrazines is conditioned by the immediate attachment of the nitrogen atoms to aryl groups, and that the phenomenon becomes more marked when positive groups are introduced into the nucleus.

*as-Diphenyldimethylhydrazine*, large, colourless prisms, m. p.  $52^\circ$ , is prepared by the action of methyl sulphate on *as*-diphenylhydrazine. It is more stable than the symmetrical isomeride, and remains unchanged when boiled for hours in xylene solution. It is more sensitive towards acids than is diphenylhydrazine, since it is converted by dilute aqueous hydrochloric acid into dimethylamine, diphenylamine, and a dye, which resembles emeraldine, and, as judged from its leuco-compound,  $\text{C}_{26}\text{H}_{23}\text{N}_3$ , m. p.

175—176°, is composed of a molecule of diphenyldimethylhydrazine united with a molecule of diphenylamine.

Attempts to prepare tetramethylhydrazine are described, but the alkylation of hydrazomethane dihydrochloride by methyl-alcoholic sodium hydroxide solution and methyl iodide only leads to the production of *N-methyl-N'-trimethylhydrazonium iodide*,  $\text{NHMe} \cdot \text{NMe}_3\text{I}$ , colourless prisms, m. p. 226·5°.

*Tetrabenzylhydrazine*, large, colourless prisms, m. p. 139·5°, is prepared by the action of benzyl bromide on tribenzylhydrazine. It does not yield salts. It is unaffected by protracted treatment with zinc dust and acetic acid, or by solution in concentrated sulphuric acid. When distilled under diminished pressure (260°/32 mm.), a portion passes over unchanged, whilst the remainder is decomposed into dibenzylamine and benzylbenzylideneamine. It is smoothly converted by concentrated hydrochloric acid at 160° into benzyl chloride and hydrazine.

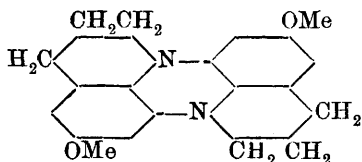
[With FRL. E. HAAS.]—Attempts to convert dicyclohexylamine into tetracyclohexylhydrazine were not successful, since a solution of the base in acetone was found to be fairly smoothly converted by permanganate into the cyclohexylamide of adipic acid,  $\text{C}_6\text{H}_{11} \cdot \text{NH} \cdot \text{CO} \cdot [\text{CH}_2]_4 \cdot \text{CO}_2\text{H}$ , colourless needles, m. p. 138—139°, which was identified by hydrolysis to adipic acid and cyclohexylamine.

It is shown that two diphenylamino-radicles can be very firmly united by the carbonyl group, since tetraphenylcarbamide remains unchanged when heated to 210°, and, in part, sublimes unaltered when directly distilled.

H. W.

**Ditertiary Hydrazines. XXIV. Ditertiary Hydrazines of the Quinoline Series.** HEINRICH WIELAND and EMMY HAAS (*Ber.*, 1920, **53**, [B], 1336—1343).—The similarity in properties between tetrahydroquinoline and monoalkylated anilines has led the authors to attempt to obtain substances in which two quinolyl residues are united by the nitrogen bond, and thus have a formal likeness to the ditertiary hydrazines. These substances are readily obtained by the direct oxidation of tetrahydroquinoline, methyltetrahydroquinoline, and *p*-methoxytetrahydroquinoline with potassium permanganate; a similar compound could not, however, be isolated in this manner from tetrahydroisoquinoline. The new “quinolinehydrazines” show little tendency towards dissociation, and give colourless solutions in boiling xylene; in solvents of higher boiling point, such as ethyl benzoate, the formation of yellow or brown solutions indicates the occurrence of dissociation, but this only takes place under such conditions that the free radicles are extensively decomposed. They are not basic. They are more or less readily affected by acids. Thus, bistetrahydroquinonyl is rapidly decomposed by ethereal or aqueous (25%) hydrochloric acid, with the formation of tetrahydroquinoline and resinification of the other half of the molecule. When an ethereal solution of the hydrazine is shaken with 2*N*-hydrochloric acid, a

benzidine transformation occurs smoothly, which must be regarded as an intramolecular change without previous dissociation. In those cases in which, for constitutive reasons, a benzidine transformation is impossible, total fission occurs; the latter type of change has been most closely studied with bis-1:2:3:4-tetrahydro-6-methoxyquinonyl, which is shown to yield 6-methoxy-1:2:3:4-tetrahydroquinoline (thallin) and thalloperazine (annexed formula).



The following compounds are described: *bis*-1:2:3:4-tetrahydroquinonyl,  $C_9H_{10} \cdot N \cdot N \cdot C_9H_{10}$ , large, yellow prisms, m. p. 141—142°; *tetrahydroquinobenzidine* [6:6'-*bis*-1:2:3:4-tetrahydroquinonyl], colourless needles, m. p. 128—129° [*dinitrosoamine*, golden rods, m. p. 196° (slight decomp.)]; *N:N'*-*bis*-1:2:3:4-tetrahydro-6-methylquinonyl, colourless needles, m. p. 107—108°; *thallinhydrazine*, m. p. 117—118° (slight decomp.); *thalloperazine*, yellow crystals, m. p. 160°, which, when treated with ethereal hydrogen chloride, readily yields a meriquinonoid azonium salt. H. W.

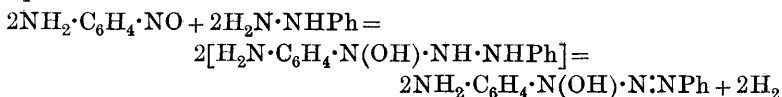
**Some Derivatives of 4-Nitro-*o*-toluidine.** ALFRED GODFREY GORDON LEONARD and AGNES BROWNE (*Sci. Proc. Roy. Dublin Soc.*, 1920, 16 [N.S.], 105—108).—When *p*-nitro-*o*-toluidine sulphate was diazotised in aqueous suspension and added to a cold alkaline solution of  $\beta$ -naphthol, 5-nitro-*o*-tolueneazo- $\beta$ -naphthol, m. p. 204°, was obtained, which dyed cotton a deep orange colour. When the nitrotoluidine was diazotised and added to *o*-toluidine hydrochloride, 5-nitro-*o*-toluenediazoamino-*o*-toluene, m. p. 133°, was obtained. 5-Nitro-*o*-toluenediazoamino-*p*-toluene, m. p. 131° (decomp.), 5-nitro-*o*-toluenediazoaminobenzene-*p*-sulphonic acid, m. p. 129° (decomp.); 5-nitro-*o*-toluenediazoamino-*p*-nitrobenzene, m. p. 118° (decomp.), and *p*-nitro-*o*-tolueneazoresorcinol, m. p. 234°, were obtained in a similar manner. W. G.

**O. Fischer's Bases from *p*-Nitrosoanilines and Arylhydrazines.** Arylazohydroxyanilides [Aryldiazohydroxyaminobenzenes]. EUGEN BAMBERGER (*Annalen*, 1920, 420, 137—169).—O. Fischer and Hepp (*A.*, 1888, 460) have described a peculiar class of substances obtained from *p*-nitrosoaniline, *p*-nitrosomonomethylaniline, and *p*-nitrosodimethylaniline on the one hand, and phenylhydrazine,  $\alpha$ -methylphenylhydrazine, and diphenylhydrazine on the other, which they have termed diazobenzenenitrosoanilines (compare Fischer and Wacker, *A.*, 1888, 1286; 1889, 702). Recently, Fischer and Johannes (*A.*, 1915, i, 907) have pointed out that these compounds are simply the *p*-amino-substitution products of the diazoxyaminobenzenes obtained by Bamberger (*A.*, 1918, i, 20; 1899, i, 589) by the con-

densation of diazonium salts with  $\beta$ -phenylhydroxylamine, and are best represented by one of the following formulæ:



or  $\text{NR}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \begin{array}{c} \diagup \text{O} \diagdown \end{array} \text{N} \cdot \text{NPhR}'$ . The latter substances are obtained also from nitrosobenzenes and phenylhydrazines, and the formation of Fischer's bases is probably represented by the equations



and  $\text{H}_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NO} + 2\text{H}_2 = \text{C}_6\text{H}_4(\text{NH}_2)_2 + \text{H}_2\text{O}$ . Substituted and unsubstituted nitrosoaryls yield arylazohydroxylanilides [diazohydroxylaminobenzenes] with primary arylhydrazines and arylazoanilide oxides with secondary hydrazines.

[With ALEXANDER LANDAU, K. BLASKOPF, E. HINDERMANN, and H. BÜSDORF.]—Benzenediazohydroxylamino-*p*-dimethylaminobenzene,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{OH}) \cdot \text{N} : \text{NPh}$  (Fischer and Wacker, *loc. cit.*), decomposes at different temperatures,  $113^\circ$  or  $119^\circ$ , according to the rate of heating (the *copper* salt is described); attempts to methylate it with methyl sulphate and potassium hydroxide led to the formation of tetramethyldiaminoazobenzene, and, possibly, a small amount of the desired ether, m. p.  $135\text{--}142^\circ$  (decomp.). Benzenediazohydroxylamino-*p*-aminobenzene yields a bluish-green *copper* salt, decomposing with explosion at  $186\text{--}187^\circ$ , and, when pure, yields colourless salts with acids; with potassium ethoxide solution, a yellow *potassium* salt is produced, which is hydrolysed by water.

Diazohydroxylaminobenzene is rapidly decomposed by boiling concentrated hydrochloric acid into nitrogen, phenol, and *p*-chloroaniline. When treated with potassium ethoxide and methyl sulphate, it yields acetaldehyde, benzene, and azobenzene, whilst the latter is also obtained when methyl iodide is used; it is unaffected by diazomethane. Zinc dust and acetic acid reduce it to aniline and phenylhydrazine. The presence of the hydroxyl group cannot be established by means of sulphur dioxide (as in the case of phenylhydroxylamine), since aniline and benzenediazonium sulphate are formed. *p*-Toluenediazohydroxylaminobenzene is similarly reduced to aniline and *p*-toluenediazonium sulphate.

*p*-Nitrobenzenediazohydroxylaminobenzene, from diazotised *p*-nitroaniline and phenylhydroxylamine, forms slender, pale yellow needles, which decompose at  $175^\circ$ , or at  $185^\circ$  when placed in a bath pre-heated to  $174^\circ$ ; the *potassium* and *sodium* salts are described. Attempts to prepare the methyl ether were not successful, the sole product isolated being *p*-iodonitrobenzene.

The decomposition of isomeric aryl diazohydroxylaminobenzenes,  $\text{R} \cdot \text{N}_2 \cdot \text{N}(\text{OH})\text{R}'$  and  $\text{R}' \cdot \text{N}_2 \cdot \text{N}(\text{OH})\text{R}$ , by mineral acids has been investigated in a number of cases. *p*-Toluenediazohydroxylaminobenzene, sulphur-yellow needles, which rapidly become brown on

exposure to sunlight, m. p. 130—131° (decomp.), is converted by sulphuric acid into nitrogen, *p*-cresol, and phenylhydroxylamine (or *p*-aminophenol), whilst benzenediazohydroxylamino-*p*-toluene, m. p. 123·5—124°, yields nitrogen, phenol, and *p*-tolylhydroxylamine (or toluquinol). Similarly, *benzenediazohydroxylamino-p-bromobenzene*, golden needles, grouped in clusters, m. p. 128·5°, gives nitrogen, phenol, *p*-dibromoazoxybenzene, and *p*-bromoaniline (the latter two being derived from *p*-bromophenylhydroxylamine), whilst *p*-bromobenzenediazohydroxylaminobenzene, straw-yellow needles, m. p. 154·5°, is decomposed into nitrogen, *p*-bromophenol, and phenylhydroxylamine. *p*-Toluenediazohydroxylamino-*p*-bromobenzene, greenish-yellow, matted needles, decomposing at 122—123° when slowly heated, but at 134° when placed in a bath pre-heated to 100°, is transformed by dilute hydrochloric acid into *p*-cresol, *pp'*-dibromoazoxybenzene, *o*-chloro-*p*-bromoaniline, and *p*-bromoaniline (the three substances last named being derived from *p*-bromophenylhydroxylamine), whereas *p*-bromobenzenediazohydroxylamino-*p*-toluene, greenish-yellow needles, which decompose at 151°, is decomposed by boiling dilute sulphuric acid into nitrogen, toluquinol, and *p*-toluidine.

Fuller details are given with regard to the action of phenylhydrazine on nitrosoaryls. In general, the substances are mixed in alcoholic solution at 0°, when action occurs with greater or less rapidity, accompanied by slight, but persistent, evolution of gas. In this manner, nitrosobenzene and phenylhydrazine yield diazohydroxylaminobenzene, phenylhydroxylamine, and, probably, azobenzene. *p*-Tolylhydrazine gives *p*-toluenediazohydroxylaminobenzene and phenylhydroxylamine, whilst the isomeric anilide and *p*-tolylhydroxylamine are obtained from *p*-nitrosotoluene and phenylhydrazine. *p*-Bromonitrosobenzene and phenylhydrazine yield benzenediazohydroxylamino-*p*-bromobenzene and *p*-bromophenylhydroxylamine (or *pp'*-dibromoazoxybenzene and *p*-bromoaniline).  
H. W.

**Does Gliadin contain Amide Nitrogen ?** THOMAS B. OSBORNE and OWEN L. NOLAN (*J. Biol. Chem.*, 1920, **43**, 311—316).—Boiling gliadin with 1% hydrochloric acid for two hours yields almost as much ammonia as boiling for twenty-four hours with 20% acid. The slight increase in free amino-nitrogen after boiling with the dilute acid shows that a very slight hydrolysis of peptide linkings occurs. Since upwards of 90% of the ammonia is yielded at a rate strictly proportional to the time of boiling, as well as the concentration of the acid, it seems fair to assume that nearly all the ammonia originates from a common group, which, like  $R\cdot CO\cdot NH_2$ , is very readily hydrolysed.

There is also an increase in acidity during the mild hydrolysis which corresponds with carboxyl groups nearly, if not quite, equivalent to the ammonia produced.

The uramino-group would appear to be present in extremely small amounts, if at all, in gliadin.  
J. C. D.

**Oxygen-capacity of Hæmoglobin.** R. WERTHEIMER (*Biochem. Zeitsch.*, 1920, 106, 12—22).—Measurements made by means of a Barcroft's differential apparatus show that, in a solution rendered alkaline by addition of sodium carbonate, 1 gram of hæmoglobin fixes at the ordinary temperature and under medium atmospheric pressure 1.33 c.c. of oxygen, which is almost the exact quantity required by Hüfner's assumption that the hæmoglobin and oxygen combine in molecular proportions (A., 1893, i, 616). With a pure, aqueous solution of hæmoglobin, the proportion of oxygen combined is about 7% less than that given above.

T. H. P.

**A New Hæmatin-like Crystalline Substance.** S. PARTOS (*Biochem. Zeitsch.*, 1920, 105, 49—59).—By heating defibrinated blood containing 1% of sodium sulphate, pressing the coagulum, washing it with hot water, again pressing it, and extracting with 92% methyl alcohol containing 3% of formic acid, the author has obtained a substance crystallising mostly in short needles. In some of its characters, this substance agrees with hæmatin, but it contains only 7.41—8.00% of iron, whereas hæmatin contains 8.9%; furthermore, the maxima of light-absorption in the two cases do not correspond.

T. H. P.

**Calorimetric Investigations on Melanins. II.** FRANZ VON HOEFFT (*Biochem. Zeitsch.*, 1920, 106, 207—211).—Further observations are described supplementing those previously made (this vol., i, 686).

T. H. P.

**Hydrolysis of Nucleotides.** M. YAMAGAWA (*J. Biol. Chem.*, 1920, 43, 339—353).—Early in the work on nucleotides, it was observed that these compounds differed from one another in their resistance to hydrolysis.

Since it is possible that the nucleotides differ in the position at which the phosphoric acid radicle is attached to the carbohydrate group, it was decided to compare the rates of hydrolysis of a number of these compounds (compare this vol., i, 712). In only one compound of this type, inosic acid, is the position of the phosphoric acid known, namely, linked to the fifth carbon atom. The rates of hydrolysis by 0.1*N*-sulphuric acid at 100° in a sealed tube were studied. The unimolecular law was followed, and the following constants, *K*, were obtained:

	<i>K</i> .
Nucleic acid .....	130 (10 <sup>-2</sup> )
Guanosinephosphoric acid .....	177 (10 <sup>-2</sup> )
Adenosinephosphoric acid .....	166 (10 <sup>-2</sup> )
Uridinephosphoric acid .....	480 (10 <sup>-3</sup> )
Inosic acid.....	470 (10 <sup>-3</sup> )
Hexathymidinediphosphoric acid .....	726 (10 <sup>-3</sup> )

Thus the velocity-constants of the guanosinephosphoric and the adenosinephosphoric acids are identical. On the other hand, the constants of inosic and uridinephosphoric acids are also identical,

in spite of the fact that their basic component is of a different nature.

J. C. D.

**Structure of Yeast-nucleic Acid. Ammonia Hydrolysis: the so-called Trinucleotide of Thannhauser and Dorfmueller.** P. A. LEVENE (*J. Biol. Chem.*, 1920, 43, 379—382).—A previous communication (this vol., i, 193) has dealt with the theoretical arguments against the conception of the structure of yeast-nucleic acid suggested by Thannhauser and Dorfmueller (*A.*, 1918, i, 47). In order to support these criticisms with evidence obtained from actual experiment, the author has shown that the conditions of hydrolysis employed by Thannhauser and Dorfmueller are such as to produce a mixture of mononucleotides, and not a trinucleotide.

J. C. D.

**The Occurrence of Optical Antipodes in Nature.** HANS PRINGSHEIM (*Ber.*, 1920, 53, [B], 1372—1374).—In a recent communication, Hess and Weltzien (this vol., i, 328) have adduced arguments which lead them to the conclusion that a fundamental difference exists between chemical processes in the vegetable and animal kingdoms, and that whereas the animal organism only builds and degrades asymmetrically, and hence involves enzymes of asymmetric structure, the vegetable organism can also build symmetrically, and hence involve symmetrical enzymes. The author considers this statement to be too general, and points out that racemic substances are also formed, if exceptionally, in the animal organism, and cites, as example, the occurrence of *dl*-arabinose in certain urines. On broader grounds, he considers that the specific action of an enzyme is only conditional, and that whilst a ferment preferentially attacks one modification of a given compound, it can, in case of necessity, also attack the antipode. So rigid a classification of symmetrical and asymmetrical ferments does not appear to have been attempted previously, and until more is known of the chemical structure of ferments, it appears too early to assume that steric arrangements must of necessity be present in them as in the substrates.

H. W.

**The Ability of Plants to Form Optical Antipodes.** KURT HESS (*Ber.*, 1920, 53, [B], 1375—1378. Compare Hess and Weltzien, this vol., i, 328).—A reply to Pringsheim (preceding abstract). Although noting that exceptions to Fischer's rule are much more common among plants and the lower organisms than among animals, the author admits that his suggestion of a "fundamental difference between the vegetable and the animal organism" is possibly too general. He considers, however, that there is abundant evidence of the asymmetric molecular structure of enzymes, and supports his contention by arguments based on the work of van't Hoff, E. Fischer, Bredig, Rosenthaler, and Bourquelot and Bridel.

H. W.

**The Chemical Nature of Enzymes.** TH. BOKORNY (*Biochem. Zeitsch.*, 1919, 100, 100—113).—The alkylamino-nitrogen was

estimated in a number of well-known enzymes by means of nitrous acid. The amino-nitrogen was found to vary from 3.05% in rennet to 7.66% in papayotin. The author considers that the results obtained are in favour of the theory of the protein nature of enzymes.

S. S. Z.

### Destruction of Rennet and Pepsin by Alkali.

L. MICHAELIS and M. ROTHSTEIN (*Biochem. Zeitsch.*, 1920, 105, 60—87).—The method used to arrive at a quantitative measure of these two enzymes consists in determining by trial that dilution of the enzyme solution which corresponds in its activity with a control solution prepared so as to be readily reproducible. The action was measured by means of the coagulation of milk containing calcium chloride in the case of rennet, and by the gradual clearing of an albumin solution rendered turbid by addition of sulphosalicylic acid in the case of pepsin.

If the hydrogen-ion concentration of a rennet solution is adjusted by means of a mixture of phosphates, the enzyme remains practically unrestricted with an acid reaction down to  $p_H=6$ . As neutrality is approached, a rapid destruction of the enzyme suddenly begins, the velocity of the destruction quickly becoming immeasurably great as the value of  $p_H$  diminishes further. For a given value of  $p_H$ , the destruction of rennet is not a unimolecular reaction, the velocity of the destruction at any moment being proportional to the 1.5th power of the amount of enzyme still present; the course of the destruction is not influenced by the enzyme already destroyed. For a given quantity of enzyme, the velocity of the destruction is proportional inversely to the fourth power of the  $H^+$ -concentration, or directly to the fourth power of the  $OH^-$ -concentration.

As regards the velocities of destruction at different temperatures ( $25.5^\circ$  and  $36.8^\circ$ ), these are identical if the solutions compared are of equal concentrations of hydroxyl ions, that is, the "physical" temperature-coefficient of the velocity is practically zero. When, however, the concentration of the hydrogen ions is the same in the two solutions, the velocity of destruction at  $36.8^\circ$  is thirty-one times that at  $25.5^\circ$ , so that the "physiological" temperature-coefficient is of considerable magnitude. From the purely physical point of view, the former method of formulation is the more correct, since the hydroxyl ions represent the destroying agency; the other method is, however, of the greater physiological importance, because in the fluids of the body the concentration of the hydrogen ions, but not that of the hydroxyl ions, is almost independent of the temperature.

Destruction of pepsin by hydroxyl ions always proceeds proportionally to that of rennet, no disproportionality being observable, even after partial adsorption of the enzyme solution by kaolin. The kinetics of the reaction is expressed empirically by the equation  $-dx/dt = k \cdot x^{\frac{1}{2}} \cdot [OH']^4$ , where  $x$  represents the quantity of enzyme present at time  $t$ .

T. H. P.



**The Influence of Neutral Alkali Salts on Diastatic Enzymes. I.** AMANDUS HAHN and KARL HARPUDE (*Zeitsch. Biol.*, 1920, **71**, 287—301).—The optimum H-ion concentration for the activity of ptyalin is  $p_H = 6.4-6.5$ , and for that of malt diastase  $p_H = 4.7$ . The enzymic activity is not only influenced by the H-ion concentration of the buffers, but by the concentration of the other ions contained in them. The combination of neutral alkali salts with the buffers produces either an accelerating or inhibiting influence, according to the reaction and concentration of the salts and buffers, on the activity of the enzymes. The optimum H-ion concentration is also changed by the combined influence of the neutral salts and the buffers. S. S. Z.

**The Influence of Neutral Alkali Salts on Diastatic Enzymes. II.** AMANDUS HAHN and KARL HARPUDE (*Zeitsch. Biol.*, 1920, **71**, 302—310).—Neutral alkali salts move the isoelectric point of ptyalin and malt diastase in the acid direction. The influence of sodium salts in this respect is more marked than that of potassium salts. The mode of action of the above enzymes is independent of their electrical nature. S. S. Z.

**The Process of Purifying Pancreatic Amylase.** H. C. SHERMAN, I. D. GARARD, and V. K. LAMER (*J. Amer. Chem. Soc.*, 1920, **42**, 1900—1907).—A further study of the process of purification of pancreatic amylase previously described (compare A., 1911, i, 827), a determination of the total solids and enzyme activity being made at each stage. It was found that alcohol up to 5%, or an alcohol-ether mixture up to 8%, of the volume of the substrate did not materially affect the activity of the pancreatic amylase. When extracts of pancreatin in 50% alcohol were precipitated by an alcohol-ether mixture, the residual solution contained about 1% of the active amylase and 2.5% of the solids of the original pancreatin, or about 5% of the solids originally extracted. When this precipitate was dispersed in water and mixed with alcohol, the filtrate showed no amylolytic activity, although it contained 25% of the solids originally extracted. In the process of purification used, about 50% of the amylolytic activity was lost by the end of the dialysis, but by using liquid-air cooling, it was possible in other experiments considerably to increase the proportion of active amylase recovered in the final product. The precipitate ("sac precipitate") which formed in the inner solution during dialysis showed very high proteolytic and little or no amylolytic activity. W. G.

**Influence of Neutral Salts on Ferment Action.** S. M. NEUSCHLOSZ (*Pflüger's Archiv*, 1920, **181**, 45—64; from *Chem. Zentr.*, 1920, iii, 355. Compare this vol., i, 698).—Investigation of the influence of neutral salts, singly and in conjunction, on the fission of sucrose by invertase on the one hand and on the surface tension of invertase solutions on the other, leads to the conclusion that the restrictive action of neutral salts on fermentative activity depends on a diminution of the dispersivity and of

the active surface of the ferment. The antagonism of ionic actions towards fermentation is shown in the diminution of the coefficient,  $K$ , of the adsorption isotherm for the action of cations in mixtures of salts; when the antagonism is maximal, this has its minimal value.  
H. W.

**Decomposition of Tyrosinase into Components.** HUGO HAEHN (*Biochem. Zeitsch.*, 1920, **105**, 169—192).—Further experiments have been made in order to ascertain to what salts the activating effect of the ash of the ultra-filtrate on  $\alpha$ -tyrosinase is due (compare this vol., i, 102).

The action of tyrosinase proceeds best when the reaction of the solution is approximately neutral, hydroxyl ions and the hydrogen ions of acetic, lactic, and hydrochloric acids exerting a retarding influence. Salts of a number of metals have been investigated, and it is found that zinc, cadmium, and calcium ions cause the most marked activation of  $\alpha$ -tyrosinase, and surpass in their action the ash of the ultra-filtrate itself. The phosphoric anion also strongly activates  $\alpha$ -tyrosinase. The latter is an organic substance which undergoes decomposition only at  $80^\circ$ , and is not decomposed by proteolytic enzymes.

Tyrosinase must be regarded as a mixture of enzymes. According to various investigators, the tyrosine is first decomposed by means of the aminoacidase in the sense of Strecker's equation, the phenolase then introducing a hydroxyl into the benzene nucleus. Subsequently, the melanin molecule is developed by the action of condensing enzymes, these being activated by metallic salts. It is to such salts that melanin owes its characteristic coloration.

T. H. P.

**Organic Compounds of Arsenic. I. Reaction between the Grignard Reagent and Arsenious Chloride.** KAORU MATSUMIYA (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 217—223).—When arsenious chloride acts on magnesium phenyl bromide in ethereal solution in equimolecular proportions, the product is triphenylarsine if the former is added gradually to the latter. If, however, magnesium phenyl bromide is added to arsenious chloride, the product is diphenylchloroarsine. Under similar conditions, magnesium  $\alpha$ -naphthyl bromide gives *tri- $\alpha$ -naphthylarsine*, m. p.  $248^\circ$ , and *di- $\alpha$ -naphthylchloroarsine*, m. p.  $116$ — $117^\circ$ , respectively.

W. G.

**The Theory of Electrolytic Ions. XVII. The Conductivity of the Sodium Arsinates.** RICHARD LORENZ and ERIKA SCHMIDT (*Zeitsch. anorg. Chem.*, 1920, **112**, 209—220).—The conductivities of the sodium salts of a number of substituted phenylarsinic acids have been measured at dilutions from 23 to 1024, and the limiting conductivities at infinite dilution have been calculated from the two Kohlrausch extrapolation formulæ,  $\mu_\infty - \mu = a[S_0]^{\frac{1}{2}}$  and  $\mu_\infty - \mu = b[S_0]^{\frac{1}{2}}$  (compare this vol., ii, 6). The smallest conductivities were shown by the neutral monosodium salts of amino-substituted acids, for example, sodium arsanilate,

*o*-aminotolylarsinate, *oo'*-diaminodiphenylarsinate, and dimethylaminophenylarsinate, the mono-acid salts of bivalent acids, such as dichloro- and dibromo-hydroxyphenylarsinic, *m*-dihydroxyphenylarsinic, and the di-acid salt of 3-nitro-4-hydroxyphenylarsinic acid ( $\mu_{\infty} = 75-100$ ). A second group,  $\mu_{\infty} = 100-200$ , comprised the neutral salts of bivalent acids, such as those mentioned above and the mono-acid salts of tribasic acids. Higher conductivities were shown by the neutral salts of the tribasic acids, 3-nitro-4-hydroxyphenylarsinic acid (329) and dinitrohydroxyphenylarsinic acid (330), by the mono-acid salt of phenylene-1:4-diarsinic acid (287), and the neutral salt of the same acid (392). The aminophenylarsinic acids are probably monobasic through internal ring formation between the amino-group and the arsinic acid residue.

E. H. R.

### Compounds of Arsenic Acid and Catechol. II.

R. F. WEINLAND and J. HEINZLER (*Ber.*, 1920, **53**, [B], 1358—1368).—The authors have described previously the preparation of catechol semiarsenate,  $\text{AsO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH})_3\cdot 4\text{H}_2\text{O}$ , and certain of its salts (A., 1919, i, 442); additional compounds of the acid are now discussed.

Catechol semiarsenate forms rhombic bipyramidal crystals,  $a:b:c = 0.958:1:0.988$  (the *dihydrate*, dimethyl alcoholate, colourless rods, and diethyl alcoholate, long, colourless, flat prisms, are described); the free acid is hydrolysed by water, about 36% of the substance being present unchanged in 5% aqueous solution. The following salts are described, in which (as in the previous examples) the acid is monobasic unless the contrary is specifically stated: *lithium* salt (+  $4\text{H}_2\text{O}$ ), shining, stout, four-sided plates; *mercurous* salt,  $\left[\text{AsO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O})_3\right]_{\text{H}}^{\text{Hg}_2}$ , dark brown, crystalline powder, which becomes yellowish-brown on exposure to air, owing to the absorption of about 1% of water; *thallium* salt, ice-like crystals; *chromium* salt (+  $12\text{H}_2\text{O}$ ), greenish-black cubes; *aluminium* salt (+  $12\text{H}_2\text{O}$ ), cubes; *cerium* salt (+  $15\text{H}_2\text{O}$ ), colourless needles; *lanthanum* salt (+  $15\text{H}_2\text{O}$ ), colourless needles; *ytrium* salt (+  $15\text{H}_2\text{O}$ ), colourless needles; *hexamminecobalti*-salt,  $\left[\text{AsO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O})_3\right]_{\text{H}_6}^{\text{Co}(\text{NH}_3)_6}$ , four-sided, yellowish-brown leaflets; *aquopentamminecobalti*-salt, acute, four-sided, brownish-red leaflets; *chloropentamminecobalti*-salt, short, copper-red rodlets; *aquopentamminenickeli*-salt, rhombic, lilac platelets; *monopyridine* salt, colourless, crystalline powder; *dipyridine* salt, stout, well-formed prisms, which continuously evolve pyridine; *monoquinoline* salt, yellowish-white powder (the salt is so sparingly soluble that, under definite conditions, it can be utilised in the gravimetric estimation of quinoline); *salt* with 1.5 molecules of quinoline, yellow, pointed rods; *monoaniline* salt, rods or pyramids; *dianiline* salt, stout, rectangular plates or rods; *guanidine* salt, colourless crystals resembling magnesium ammonium phosphate.

As is to be expected from its behaviour with pyridine and quinoline, catechol semiarsenate yields sparingly soluble salts with the alkaloids; this has been demonstrated in the cases of morphine, quinine, strychnine, colchicine, hydrastinine, veratrine, coniine, and apomorphine. H. W.

### Aromatic Mercuri-organic Derivatives. MORRIS S.

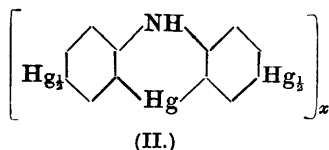
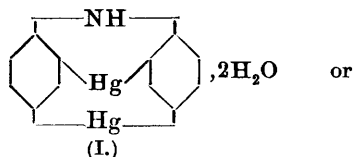
KHARASCH and JEAN F. PICCARD (*J. Amer. Chem. Soc.*, 1920, **42**, 1855—1864).—Methods are outlined for the preparation of a six-atom heterocyclic ring containing mercury in place of a non-metal. By the action of methyl sulphate on *m*-bromoaniline in the presence of sodium carbonate, a mixture of *m*-bromomethylaniline and *m*-bromodimethylaniline was obtained, from which, by treatment with sodium nitrite and hydrochloric acid, *m*-bromo-*p*-nitrosodimethylaniline and *m*-bromophenylmethylnitrosoamine, m. p. 49°, were obtained. By reduction with stannous chloride and hydrochloric acid, *m*-bromo-*p*-nitrosodimethylaniline yielded *m*-bromodimethyl-*p*-phenylenediamine dihydrochloride, giving the free base, m. p. 47·5°. The free base, when mixed with *m*-bromodimethylaniline and the mixture oxidised with potassium dichromate in hydrochloric acid solution, gave, on the addition of zinc chloride, *oo'*-dibromo-Bindschedler's green,  $C_{32}H_{38}N_6Br_4Cl_2 \cdot ZnCl_2$ , from which,

by addition of mercuric chloride, the double mercuric chloride salt (annexed formula) was obtained.

*m*-Bromophenylmethyl-nitrosoamine, when dissolved in a mixture of ether and alcohol and the solution saturated with hydrogen chloride, underwent molecular rearrangement, giving *m*-bromo-*p*-nitrosomethylaniline hydrochloride, m. p. 168°, from which the free base was obtained.

*o*-Chloromercuriphenol, when treated with nitrous acid, yielded *p*-nitroso-*o*-chloromercuriphenol,  $OH \cdot C_6H_3(NO) \cdot HgCl$ , which, when warmed with ammonium chloride, ammonium acetate, and ammonium carbonate, gave *p*-nitroso-*o*-chloromercurianiline.

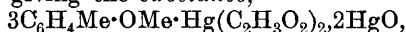
When heated with mercuric chloride, diphenylamine yielded tetrachloromercuridiphenylamine,  $NH[C_6H_3(HgCl)_2]_2$ , from which, by the action of sodium thiosulphate, 3:3'-mercurimercazine (formula I or II) was obtained.



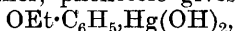
When tetrachloromercuridiphenylamine was warmed with a mixture of sulphuric and nitric acids, dinitro-2:2':3-trichloromercuridiphenylamine was obtained, which, by the action of sodium thiosulphate, yielded mercury-bis-3-dinitro(?)-mercazine. W. G.

**Mercuration. V. Mercuration of Phenol Ethers.** W. MANCHOT and F. BÖSSENECKER (*Annalen*, 1920, **421**, 331—345). —Volhard and Dimroth have shown that the mercuration of derivatives of benzene occurs in such a manner that a hydrogen atom attached to the ring is replaced by the group  $\text{HgX}$ . The authors' work on the mercuration of ethylene and its derivatives has, however, rendered it not improbable that the primary products are additive compounds. Experiments with various phenol ethers tend to show that such is actually the case. The products obtained with mercuric acetate vary with the particular ether used, but may be classified as more or less completely hydrolysed additive compounds. They are readily decomposed by treatment with warm dilute hydrochloric acid, and are immediately converted by alkali haloids into products which are mercurated in the nucleus.

*p*-Tolyl methyl ether slowly reacts with aqueous mercuric acetate solution at  $50^\circ$ , giving the *substance*,



thin, colourless needles, m. p.  $132\text{--}133^\circ$ , immediately transformed by sodium chloride solution into the *product*,  $\text{C}_6\text{H}_3\text{Me}\cdot\text{OMe}\cdot\text{HgCl}$ , colourless needles, m. p.  $162^\circ$ . Similarly, anisole yields the *compound*,  $\text{C}_7\text{H}_8\text{O}\cdot\text{Hg}(\text{OH})_2$ , slender needles, m. p.  $173^\circ$ , which forms anisole when treated with dilute hydrochloric acid, and *p*-anisylmercuri-chloride, m. p.  $236\text{--}237^\circ$ , under the action of sodium chloride. In like manner, phenetole gives the *substance*,



small, matted needles, m. p.  $135\cdot5^\circ$ , which is converted by potassium bromide into *p*-phenetylmercuri-bromide, needles, m. p.  $238^\circ$ .

H. W.

### Physiological Chemistry.

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#### Hydrogen-ion Measurements on Blood in the Neighbourhood of the Isoelectric Point of Hæmoglobin.

T. R. PARSONS and WINIFRED PARSONS (*Proc. Physiol. Soc., J. Physiol.*, 1920, **53**, c—cii).—The view having been elaborated that, under physiological conditions, hæmoglobin is an acid of sufficient strength to expel carbon dioxide from sodium hydrogen carbonate at low tensions of the gas, it became of interest to observe the changes in its acid properties as the reaction of the medium in which it occurs approaches the isoelectric point. There is a sudden increase in carbon dioxide combining power in completely reduced hæmolyzed blood, similar to that noted by Straub and Meier (*A.*, 1918, ii, 467; 1919, i, 53) in acidified oxygenated whole and hæmolyzed blood at a certain hydrogen-ion concentration not far removed from neutral point.

Hydrogen-ion measurements were made at various tensions of carbon dioxide, and these results show that over a certain range, depending on the exact amount of lactic acid present, the hydrogen

ion of the hæmolyzed blood remains constant. It therefore appears that during this sudden increase of carbon dioxide combining power near the neutral point, the extra carbon dioxide is taken up in the form of sodium carbonate, and does not combine directly with hæmoglobin.

The reason why one molecule of extra carbon dioxide corresponds with each molecule of hæmoglobin seems to be that each hæmoglobin molecule is parting with one atom of available sodium for the formation of bicarbonate. It should be noted that this region of constant hydrogen-ion concentration is still on the alkaline side of the isoelectric point of hæmoglobin.

J. C. D.

**Occurrence of Creatinine and Creatine in the Blood in Healthy and Pathological Cases. IV. Revision of Previous Methods and Results.** JOH. FEIGL (*Biochem. Zeitsch.*, 1920, 105, 255—281. Compare A., 1918, i, 202, 357).—The considerations here presented show that the numbers obtained by Folin's older method for the proportion of pre-formed creatinine in the blood are to be regarded as trustworthy, but that the results obtained by American and German investigators for creatine are valueless. Revised procedure is described, and new results given for blood of healthy and diseased subjects.

T. H. P.

**The Appearance of Aldehyde-like Substances in the Blood of Six Persons (Diabetes Mellitus, Diseases of the Kidneys).** WILHELM STEPP (*Biochem. Zeitsch.*, 1920, 107, 60—80).—The presence of substances possessing the properties of aldehydes was established in the blood of some diabetic, nephritic, and other patients. These substances form iodoform with iodine in alkaline solution, and reduce Fehling's solution as well as ammoniacal silver, and give a red coloration with magenta-sulphurous acid. They are destroyed on being heated with silver oxide. In certain cases, the Rimini reaction was also obtained. The above reactions were also obtained from distillates in alkaline solution.

S. S. Z.

**Physiology of Blood Sugar. III. The Residual Reduction of Blood.** RICH. EGE (*Biochem. Zeitsch.*, 1920, 107, 229—245. Compare A., 1918, i, 356; ii, 278).—The residual reducing capacity of blood can be estimated by fermenting the reducing sugars with yeast. The reducing capacity of the yeast, as well as its activity, must be taken into consideration. The residual reduction of blood as estimated by Bang's micro-method is extremely small, and is of the same order in the plasma as in the corpuscles. Arterial and venous blood also show the same residual reduction.

S. S. Z.

**The Chemistry of the Blood-colouring Substances.** E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1919, 100, 64—80).—According to the authors, there is only one substance, *haemochrome*, which is responsible for the colour of blood. It is an amorphous powder, which exists in colloidal solution in water. In alcohol and bicarbonate, on the other hand, it exists in real

solution. The spectroscopic behaviour of hæmochrome is influenced by the solvent in which it is dissolved. Hæmoglobin is hæmochrome adsorbed by globin.

S. S. Z.

### **The Biochemistry of Phosphatides and Sterols. I**

R. BRINKMAN and (FRL.) E. VAN DAM (*Biochem. Zeitsch.*, 1920, 108, 35—51).—The osmotic resistance of blood corpuscles raised by washing them with a physiological salt solution (0·85% NaCl) is due to the removal of the adhering lecithin, which is adsorbed by them from the plasma, and which is responsible for lowering their osmotic resistance. Cholesterol has the opposite effect. An isotonic sucrose solution does not remove the adhering lecithin. The analogy between the properties of the plasma lecithin and the serum complement, as well as its relation to the middle piece of the complement, is discussed. A method for the estimation of the osmotic resistance of the corpuscles under various conditions is described.

S. S. Z.

### **The Biochemistry of Phosphatides and Sterols. II. The Importance of Cholesterol for the Physico-chemical Properties of Cell Surface.**

R. BRINKMAN and (FRL.) E. VAN DAM (*Biochem. Zeitsch.*, 1920, 108, 52—60).—It has been pointed out by Hamburger (*Pflüger's Archiv*, 1895, 141, 230) and others that erythrocytes in salt solutions become spherical. The authors show that the slightly negative charge of the corpuscle is augmented by being in contact with the charged slide, and this increase in the charge is responsible for the change in form of the erythrocyte. In the plasma the corpuscles are surrounded by a layer of lecithin containing cholesterol in colloidal solution, which prevents the cell from being acted on by an electric charge, and therefore their shape is not altered.

S. S. Z.

### **The Biochemistry of Phosphatides and Sterols. III. The Significance of the Functional Antagonism between Phosphatides and Cholesterol.**

R. BRINKMAN and (FRL.) E. VAN DAM (*Biochem. Zeitsch.*, 1920, 108, 61—73).—Phosphatides and sterols are always present in the animal organism in definite proportions, because they function antagonistically to each other. The relative amounts of cholesterol and lecithin influence the resistance of the corpuscles, the electrical isolation of the cells, the permeability to ions of the cell surface, and the water content of the tissues. The change in quotient of these two constituents, especially through the agency of nutrition, is of importance. A one-sided administration of lecithin to a rabbit has produced intensive hæmolysis in vivo, as well as regeneration of the blood corpuscles.

S. S. Z.

### **Action of Electrolytes on Ricin-Hæmagglutination.**

PETER RONA and PAUL GYÖRGY (*Biochem. Zeitsch.*, 1920, 105, 120—132).—The results of the authors' experiments show that the agglutination of blood corpuscles by ricin takes place solely in presence of electrolytes. The cations may be arranged in the



following series, the first having the least and the last the greatest effect on the agglutination: K, Na, Ba, also Mg, Ca. Contrary to the statements of various authors, the agglutination is influenced differently by different anions; in the series Cl, SO<sub>4</sub>, NO<sub>3</sub>, phosphate anion, FeCy<sub>6</sub>, SCN, I, the first aids agglutination the most and the last the least. The results obtained are in agreement with Freundlich and Rona's theory, according to which the sensitisation of blood corpuscles depends on diminution of their electric charge. Roughly quantitative investigation of the cataphoretic velocities of blood corpuscles charged with ricin, and others uncharged, appeared to indicate no certain difference between these velocities.

T. H. P.

**Preparation and Investigation of Thrombin.** MAX BLEIBTREU and EDGAR ATZLER (*Pflüger's Archiv*, 1920, 181, 130—140; from *Chem. Zentr.*, 1920, iii, 420).—Acetic acid is added to the serum (100 c.c.), which has been agitated with casein (1 gram), whereby the latter is precipitated, together with the adsorption compounds which it forms, with thrombin and metathrombin. The preparation is stable when dried and powdered, and does not lose its activity when preserved during a year. Active and stable thrombin solutions can be prepared from it by treatment with water and *N*-sodium hydroxide solution, neutralisation with *N*-hydrochloric acid, and purification by precipitation with colloidal ferric hydroxide, saturated magnesium sulphate solution, and alcohol (one-third to one-half volume), and these solutions have been found useful in treating hæmorrhage in animals. In an electric field, thrombin and metathrombin migrate to the anode.

H. W.

**Mechanism of Pepsin Action.** A. GYMANT (*Biochem. Zeitsch.*, 1920, 105, 155—168).—The author discusses the two principal theories of the action of pepsin, especially that according to which the function of the acid is to cause the protein to swell, and so become accessible to the enzyme. When hydrochloric acid is used, the "protein chloride" is usually a strongly dissociated electrolyte, so that, as the acidity increases to a moderately high value, the number of protein ions and the swelling must increase. This is, however, not always the case, since with serum albumin + sulphosalicylic acid, and with ricin globulin + sulphosalicylic acid, the acid causes, not swelling, but precipitation, of the protein. Digestion experiments with the heterogeneous systems thus obtained show that the optimal acidity is  $n_{\pi}=1.7-2$ ; this optimum coincides with that observed with dissolved protein, although, if the swelling had any influence, displacement of the optimum would be expected. Further experiments show that the whole course of the digestion curve, as well as the position of the optimum, may be attributed solely to the concentration of the hydrogen ions by virtue of their simultaneous actions on the protein and on the pepsin. The position of the optimal hydrogen-ion concentration is never affected by the nature of the anion of

the acid, but this may in some cases, for instance, with sulphosalicylic acid, influence the absolute amount of digestion.

T. H. P.

**The Significance of Gastric Hydrochloric Acid, and the Importance of the H-ion Concentration in Biological Sciences.** I. TRAUBE (*Biochem. Zeitsch.*, 1920, 107, 295—299).—A theoretical paper.

S. S. Z.

**The Problem of Nuclein Metabolism. The Formation of Uric Acid after Parenteral Administration of Purine Nucleosides in Healthy Men.** JULIUS ROTHER (*Zeitsch. physiol. Chem.*, 1920, 110, 245—253).—A rise was observed in the uric acid excretion of patients who previously received an intramuscular injection of guanosine. The author points out that, as the treated patient manifested high temperatures and other abnormal symptoms, it is possible that the increase in the uric acid may not have been due entirely to the decomposition of the guanosine, but may have been produced endogenously, owing to the disturbed condition of the patient.

S. S. Z.

**Intermediate Metabolism and its Active Enzymes.** TORSTEN THUNBERG (*Skand. Arch. Physiol.*, 1920, 40, 1—91; from *Chem. Zentr.*, 1920, iii, 390—391).—The severed muscular tissue of a recently killed frog, after being extracted with water, loses the power of decolorising methylene-blue in a medium free from oxygen; this capacity can, however, be restored by the addition of certain substances, since, under the action of an enzyme, two atoms of hydrogen are removed from the latter and transferred to the dye, with consequent formation of its leuco-base. The cells are provided with an enzyme which is specifically active towards those substances which activate the decolorising capacity, and these substances therefore probably represent intermediate stages through which the primary simple nutrient materials pass in their transformation into the final products. The author therefore considers materials such as dextrose, fats, amino-acids, etc., to undergo a series of transformations by indirect oxidation effected by "dehydrogenation." The newly discovered enzymes, in their capacity as "hydrogen transportases," bring about the removal of hydrogen from the nutrient material, which either combines with oxygen or is employed in the halogenation of other substances. According to this conception, all nutrient material, no matter of how diverse a character, must be able to yield hydrogen. The latter is the universal fuel for all cells. The replaceability of one food by another is therefore regarded in a new light.

The following substances act as powerful restorers of the lost decolorising power: formic, acetic, butyric, hexoic, succinic, fumaric, maleic, tartronic, *l*- and *dl*-malic, *l*-, *r*-, and *meso*-tartaric, *l*- $\alpha$ -hydroxyglutaric, citric, lactic,  $\alpha$ - and  $\beta$ -hydroxybutyric, pyruvic and glutamic acids, and alanine. On the other hand, the following materials are inactive: propionic, isobutyric, isovaleric, crotonic, allylactic, oxalic, malonic, glycollic, hydroxyisobutyric, methyl-

succinic, glutaric, adipic, and a number of other saturated and unsaturated dicarboxylic acids, glycine, leucine, phenylalanine, and other amino-acids, creatine, creatinine, guanidine hydrochloride, taurine, urea, and glucosamine.

It is possible to differentiate between the various enzymes from the mixture in the muscle by powerful and rapid cooling and by increase in temperature; the enzymes which act on the different acids mentioned above show a very uneven resistance to alterations in temperature and a pronounced "cryolability." H. W.

**The Relation of Cholesterol to the Intermediate Stage of Fat Metabolism.** W. HUECK and L. WACKER (*Biochem. Zeitsch.*, 1919, **100**, 84—99).—The free and esterified cholesterol were estimated in the total blood, the serum, and in the fresh and dried erythrocytes and leucocytes in the blood of various animals. The results are given in a table. The erythrocytes are characterised by the absence of cholesterol esters. The cholesterol in animal fat was found to be present mostly, if not entirely, as free cholesterol. Cholesterol was also fed to rabbits, and the lipoid fraction of the blood was examined in these animals as well as in normal and starving rabbits. The results show a great variation in the cholesterol content of the blood of normal rabbits. An increase was found in the total lipoids, the free and esterified cholesterol, and the lecithin in the blood of the animals which received the cholesterol. Lipæmia was observed in the starved animal. S. S. Z.

**Action of the Accessory Food Factors.** FRITZ VERZÁR and JOSEF BÖGEL (*Biochem. Zeitsch.*, 1920, **108**, 185—206).—The pharmacological action of extracts of the fat-soluble *A* and water-soluble *B* accessory food factors on various organs was examined. No characteristic behaviour of these factors could be established. S. S. Z.

**Amino-acids in Nutrition. I. Studies on Proline: Is Proline a Growth-limiting Factor in Arachin (Globulin from the Pea-nut)?** BARNETT SURE (*J. Biol. Chem.*, 1920, **43**, 443—456).—The biological value of arachin as tested on rats appears to be low, but the low content of proline is not the factor limiting growth. Evidence in support of this is given by experiments, which showed that proteins rich in proline, such as zein and gelatin, do not supplement the protein arachin. Other experiments show that the low nutritive value of arachin is not raised by additions of tryptophan, cystine, a mixture of glycine, alanine, and valine, or by the sister globulin, conarachin.

Lactalbumin supplements arachin, particularly when cystine is also added. J. C. D.

**Amino-acids in Nutrition. II. The Nutritive Value of Lactalbumin: Cystine and Tyrosine as Growth-limiting Factors in that Protein.** BARNETT SURE (*J. Biol. Chem.*, 1920, **43**, 457—468).—The proteins removed from milk by coagulation,

after caseinogen has been separated, do not possess a high biological value for growth in rats. Cystine and tyrosine will raise this value and supplement the protein deficiencies. Lactalbumin is not, however, a protein with an unusually low cystine content, and this suggests that the efficiency of a protein may largely depend on its constitution as well as on its composition of amino-acids. The author suggests that the opinion expressed by Osborne and Mendel (A., 1916, i, 690), that lactalbumin is a protein of high nutritive value, is founded on experiments which are open to criticism. Evidence was obtained that organically-bound sulphur and a substance giving a Millon reaction are present to an appreciable extent in protein-free milk. J. C. D.

**Capillarisation in Biochemistry.** RUDOLF KELLER (*Biochem. Zeitsch.*, 1920, 107, 43—49).—A theoretical paper on capillary electricity. S. S. Z.

**Taste.** SHINTARO KODAMA (*J. Tokyo Chem. Soc.*, 1920, 41, 495—534).—Considering the facts that (1) optical isomerides have different taste, (2) substitutions always affect the taste, (3) all the compounds containing either Cohn's sapophore group or Oertly and Meyer's glucophore contain vibratory hydrogen, and (4) the taste of electrolytes is due to the sum of the tastes of molecular electrolyte, anions, cations, and complex ions, the author proposes a theory that the taste of organic substances is due to electric vibration of the sapophoric element. A detailed explanation, and examples with several hundreds of different compounds, are given. Applications of the theory in physiology, psychology, and medicine are suggested. Methods of preparation of different optical isomerides used for taste experiments are included in the last chapter.

CHEMICAL ABSTRACTS.

**Taste.** YRJÖ RENQVIST (*Skand. Arch. Physiol.*, 1918, 38, 97—201; from *Chem. Zentr.*, 1920, i, 591).—The taste system is composed of the sensory particles and their components and the liquid or solution; it is thus a heterogeneous system, one part of which comprises the colloidal protoplasmic taste cells or nerve terminations, and the other the liquid or solution. The main changes which occur depend on alteration of surface and electrical energy. Equally marked sensations of taste must correspond with the adsorption of equal amounts of the substance by the organs of taste. The concentration necessary to induce taste with the alkali salts is an additive function of the inverse values of the rates of migration of the ions. The concentration for barium and calcium chlorides is less than that for the alkali salts, whilst for aluminium chloride a minimum value is attained. Valency is therefore an important factor, and this appears to indicate a suspensoid character of the adsorption in the system of taste. In addition to the rate of adsorption, electrical phenomena are also important in their effect on the induction of taste by different electrolytes. The phenomena of the sensation of taste produced by homologous and isomeric compounds are explicable on the

assumption that the process is one of adsorption. Experimental investigation confirms the accuracy of a deduction, from which it appears that the sensation of taste is more persistent with increasing concentration of tasted substance and increasing adsorption exponent, and with decreasing inducing concentration and rate of diffusion. The author also examines the qualities of taste, their variation with differing concentrations of electrolyte, and their relationships to the differences of potential caused by the electrolyte in the sensory system. The quality of the induced taste can be foretold with some degree of accuracy if the rate of migration of the ions of a univalent electrolyte and its concentration are known. The "compensation of taste" is a peripheral phenomenon which is observed in the sensory system; a bitter taste is not, however, compensated. The "fundamental tastes," sweet, bitter, and sour, are chosen, from which, in analogy to the Young-Helmholtz theory of colour vision, all the various sensations of taste can be compounded.

H. W.

**The Inducing Value of the Sensation of Taste by certain Homologous and Isomeric Compounds.** YRJÖ RENQVIST (*Skand. Arch. Physiol.*, 1920, **40**, 117—124; from *Chem. Zentr.*, 1920, iii, 425—426).—The concentrations requisite to produce the sensation of taste have been estimated for six different alkyl esters of cyanoacetic acid, the methyl and ethyl esters of oxalic, malonic, and succinic acids, the homologous monohydroxy-alcohols from methyl to octyl alcohol, and various isomeric esters of certain ether acids. In the majority of cases, the results are in agreement with the relationships established previously (preceding abstract) between the inducing concentration for taste and the coefficients of diffusion. The inducing concentrations of isomerides are approximately equal, whilst with homologous compounds they diminish with increasing molecular weight. The surface tensions of isomeric substances at the inducing concentration are determined by the drop method, and found to be approximately equal.

H. W.

**Protamine from the Spermatozoa of the Japanese Mackerel, *Scomber japonicus*.** KUNIIKO SUMIKURA (*J. Tokyo Chem. Soc.*, 1920, **41**, 281—310).—Crude protamine is prepared by Kossel's method, dissolved in hot water, histone is removed by precipitation with ammonia, and the filtrate is neutralised with sulphuric acid. By adding a neutralised sodium tungstate solution, a white precipitate is obtained, which is recrystallised repeatedly and dried over sulphuric acid. This product is redissolved in hot water, and  $\frac{1}{2}$  vol. of 50% alcohol is added to obtain a white turbidity. Cooling over ice and the addition of ether give the oily substance, which, after being washed seven to eight times with water saturated with ether, is precipitated by alcohol (three times the original vol.). The precipitate is washed with alcohol-ether mixture and dried over sulphuric acid. Such protamine contains 20·31% N, 7·15% H, 36·48% C, 22·03%  $\text{H}_2\text{SO}_4$ , corresponding with

$C_{30}H_{71}O_9N_{14}, 2H_2SO_4$ , which shows less nitrogen, and more hydrogen and oxygen, than scombrin, prepared from European mackerel by Kurajev. Hydrolysis gives 0.609% of ammonia-nitrogen, 0.096% of hexone base nitrogen, 71.73% of arginine nitrogen, 17.26% of monoamino-nitrogen, on the basis of 100 parts of the total nitrogen. Lysine is absent, and the presence of histidine is doubtful. The protamines of European and Japanese mackerels are probably not identical.

CHEMICAL ABSTRACTS.

**Proteinogenous Amines. X. The Response of the Excised Uterus to Potassium, Rubidium, and Cæsium Ions.**

MILTON T. HANKE and KARL K. KOESSLER (*J. Biol. Chem.*, 1920, **43**, 579—582).—Potassium and rubidium salts in concentrations of about  $N/75$  produce tonic contraction of the virgin uterus of the guinea-pig, from which the muscle does not recover until the stimulating ions are removed.

The response with cæsium is less marked.

J. C. D.

**Lipoids. XVII. Dilignoceryl-N-diglucosamine Monophosphoric Ester, a New Diaminomonophosphatide from the Brain.**

S. FRÄNKEL and F. KAFKA (*Biochem. Zeitsch.*, 1920, **101**, 159—171. Compare A., 1914, i, 128).—Brain dried in a vacuum at a low temperature, and freed from cholesterol by extraction with acetone, was extracted with boiling light petroleum. The concentrated petroleum fraction was extracted further with absolute alcohol. A lead compound,  $C_{60}H_{111}O_{14}N_2PPb_3$ , decomposition point 305—308°, was obtained from this fraction, which, unlike Thudichum's myelin, was soluble in ether. It was also soluble in benzene, but not in alcohol. By decomposing the lead salt with hydrogen sulphide, the free compound,  $C_{60}H_{117}O_{14}N_2P$ , m. p. 190°, was obtained. On hydrolysis, lignoceric acid, glucosamine, and phosphoric acid were obtained from this compound. It is, therefore, *dilignoceryl-N-diglucosamine monophosphoric ester*.

S. S. Z.

**Unsaturated Lipoids of the Liver.**

P. A. LEVENE and T. INGVALDSEN (*J. Biol. Chem.*, 1920, **43**, 359—378).—The unsatisfactory state of the knowledge regarding the phosphatides of the liver led the authors to reinvestigate the subject. The unsaturated lipoids of other organs have been classified as (1) acetone-soluble lipoids, consisting principally of lecithin with small proportions of cephalin; (2) acetone-insoluble, but alcohol-soluble, fraction, which consists of lecithin with larger proportions of cephalin; and (3) a fraction insoluble in acetone and alcohol, which consists of very small proportions of lecithin with larger amounts of cephalin, together with substances which are derived from the lipoids themselves.

These three fractions, with their general characteristics, were obtained from liver tissue, and in this respect the lipid material obtained from the liver is similar to that obtained from the other organs. A study of the lecithin isolated from the liver reveals that there are two fatty acids in the molecule, one saturated, stearic

acid, and the other unsaturated and of the linolic series. No evidence of the presence of oleic acid was obtained.

The paper records progress in the attempts to prepare a pure specimen of cephalin. Preparations containing 70% have been obtained. J. C. D.

**Presence of a Large Amount of Cholesterol Ester in the Liver Oil of the Basking-shark, *Cetorhinus maximus*, Gunner.** MITSUMARU TSUJIMOTO (*Bull. Tokyo Ind. Research Lab.*, 1920, 15, No. 2, 1—10).—So far, an animal oil has never been reported to contain more than 3% of cholesterol. The oil extracted at 100° from the liver of a young basking-shark had  $D_{15}^{20}$  0.9176, acid number 0.301, saponification number 14.57, Wijs number 174.4,  $n_D^{20}$  1.4836, butyrefractometer at 20°, 87.2,  $[\alpha]$  -2.7, unsaponifiable matter 20.55%. It contained 9% of squalene. 42% of the unsaponifiable substance is found to be cholesterol ester, corresponding with 8.6% of original oil. More than 90% of the cholesterol exists as ester, the remainder being free. By means of lipase, this cholesterol ester was separated from other fat. Whether the presence of such a large amount of cholesterol in the oil of this shark is characteristic of this fish or is due to a peculiar pathological condition which might be associated with this particular specimen has not been yet determined.

#### CHEMICAL ABSTRACTS.

**The Monoamino-acids of the Lens of the Eye.** A. JESS (*Zeitsch. physiol. Chem.*, 1920, 110, 266—276).—The monoamino-acid content of the albumoid, the  $\alpha$ -crystallin, and the  $\beta$ -crystallin of the lens of the eye has been determined. The outstanding feature of this analysis is that the alanine content of the albumoid is low, 0.8% against 2.6% and 3.6% in the  $\beta$ -crystallin and the  $\alpha$ -crystallin respectively. Only traces of valine (0.2%) could be detected in the albumoid. One-half of leucine and its isomerides could be established in the  $\beta$ -crystallin as compared with the quantities of these substances present in the  $\alpha$ -crystallin and the albumoid. No very striking differences in the content of the other monoamino-acids of these proteins could be established. S. S. Z.

**The Capacity of the Animal Skin to React with Phenol-aldehydes.** OTTO GERNGROSS (*Biochem. Zeitsch.*, 1920, 108, 82—97).—Glycylglycine ester when treated with *o*-protocatechu-aldehyde and *o*-vanillin, respectively, yields compounds showing a golden-yellow colour similar to that obtained when skins are treated with these substances. A combination of *o*-protocatechu-aldehyde with *L*-tyrosine methyl ester yielded a similar colour. Hide powder previously treated with formaldehyde was only slightly coloured by phenolaldehydes, and this colour could be washed out. This shows that the basic groups of the skin react with the phenol-aldehydes in the ordinary way. On the other hand, treated and untreated skins gave the same coloration with sodium diazobenzene-sulphonate. The imino-group of the iminazole ring does, therefore, not react with formaldehyde. *o*-Protocatechualdehyde is capable

of tanning skins, *o*-vanillin is not. The author attributes the tanning action to the two hydroxyl groups in the benzene ring of the former compound. He also suggests the possibility that the colouring action of the phenolaldehydes is not due to the aldehyde, but to the phenol group. The colouring cannot be ascribed to the formation of a Schiff's base.

S. S. Z.

**Amino-acids of the Blood as the Precursors of Milk Proteins.** C. A. CARY (*J. Biol. Chem.*, 1920, **43**, 477—489).—In the non-lactating cow, the level of amino-acid nitrogen is approximately the same in the blood from the mammary vein and from the jugular vein. When the mammary gland is active, however, the level of amino-acid nitrogen is very much lower in the blood in the mammary vein than in the jugular. This indicates that the proteins of the milk are built up from amino-acids brought to the gland by the arterial system.

The carbon dioxide capacity of the plasma has also been studied in both conditions, but the significance of the results is uncertain.

J. C. D.

**Influence of Ether or Alcohol on the Coagulation of Milk. Influence of Sodium Nucleinate on the Coagulation of Milk and Blood.** M. DOYON (*Compt. rend. Soc. Biol.*, 1920, **83**, 918—919; from *Chem. Zentr.*, 1920, iii, 395).—The coagulation of milk by rennet is noticeably facilitated by the presence of ether or alcohol, but retarded by sodium nucleinate; the latter effect is immediately removed by addition of calcium chloride. Blood does not coagulate, but rapidly suffers very marked hæmolysis when brought directly into sodium nucleinate; in this case, also, coagulation is immediately induced by the addition of calcium chloride.

H. W.

**The Technique of Urine Acidimetry (specially for Clinical Purposes).** W. BIEHLER (*Zeitsch. physiol. Chem.*, 1920, **110**, 298—306).—The H-ion concentration of urine calculated from titration figures differs from values obtained by direct estimation of the H-ion concentration. By plotting curves from the values obtained by the two methods, it is seen that there is a relationship between the two sets of results. It is suggested that the real H-ion concentration can be obtained by titration and comparing the two curves.

S. S. Z.

**Pyrrole and Melanuria. III.** PIETRO SACCARDI (*Gazzetta*, 1920, **50**, ii, 118—128. Compare A., 1919, i, 421; this vol., i, 203).—In view of the fact that by some tyrosine and by others adrenaline is regarded as the mother substance of the melanins, the author has made experiments the results of which indicate that tyrosine alone is not capable of giving rise to melanin, since it exhibits great resistance to organic and inorganic oxidising agents; adrenaline is considerably more sensitive than tyrosine to oxidising agents, and, under the action of chlorine water, yields a brown precipitate of the appearance of melanin.



Pyrrole administered by ingestion is slowly absorbed and slowly eliminated by man, and large doses are necessary to produce melanuria, since the organism partly destroys it and partly eliminates it unchanged; when injected, pyrrole is largely oxidised.

Egg-albumin, but not dextrose, yields a true melanoidal substance when subjected to protracted boiling with concentrated hydrochloric acid.

Melanins from hair, from the choroid, and from a melanotic tumour undergo vigorous oxidation when treated with peracetic acids, and yield minute, acicular or tabular crystals, which, in view of the resemblance between the phenomena of these oxidations and those of the oxidation of pyrrole-black, may consist of succinic acid or succinimide.

T. H. P.

**The Physiological Action of Silicic Acid. The Influence of Silicic Acid on the Animal Organism.** FRANZ SCHUHBAUER (*Biochem. Zeitsch.*, 1920, **108**, 304—308).—Merck's preparation of sodium silicium purissimum is hydrolysed in the intestine by the action of water, with the formation of sodium hydroxide. This change can be obviated by neutralising the preparation.

S. S. Z.

**The Physiological Action of Silicic Acid. The Absorption of Silicic Acid.** FR. BREEST (*Biochem. Zeitsch.*, 1920, **108**, 309—316).—A rise in the silica content of the body can be established by increasing the silica in the food in a suitable form. Only a small portion of the administered silica is retained by the body. The author confirms Schuhbauer's results concerning the hydrolysis of Merck's silicates (see preceding abstract).

S. S. Z.

**Do Amino-acids Possess Secretin Characteristics?** SCHWEITZER (*Biochem. Zeitsch.*, 1920, **107**, 256—267).—Amino-acids obtained by hydrolysis of protein with hydrochloric acid at 100° have shown no definite secretin action on the gastric glands. It is concluded from some of the experiments that secretin activity is not due to a single definite chemical substance, but may be produced by various compounds.

S. S. Z.

**The Physical Theory of Pharmacological Actions.** WOLFGANG HEUBNER (*Biochem. Zeitsch.*, 1919, **101**, 54—61).—A theoretical paper in reply to Traube (this vol., i, 204).

S. S. Z.

**Pharmacological Actions of the Reduction Products of Coumarin.** K. FROMHERZ (*Biochem. Zeitsch.*, 1920, **105**, 141—144. Compare Ellinger, A., 1908, ii, 1060; Trendelenburg, *Arch. exp. Path. Pharm.*, 1915, **79**, 9, 190).—The author has investigated the action on various animals of hydrocoumaric acid, its lactone (melilotol), *o*-hydroxyphenylpropyl alcohol, and the ether of this alcohol (chroman). The results obtained show that, with the exception of hydrocoumaric acid, these compounds exhibit approximately the narcotic properties of coumarin, but show no

advantages, especially as regards the ratio of toxicity to activity, over the parent substance. Further, Fränkel's view ("Arzneimittelsynthese"), that coumarin is a substance which exerts narcotic effects in virtue of its carbonyl group, is contradicted, since reduction of the carbonyl to methylene does not remove the narcotic properties. Comparison of hydrocoumaric acid with melilotol appears to indicate that the lactone ring is of significance as regards narcotic action, but this indication fails when the lower stages of the reduction are reached. T. H. P.

**Quantitative Studies in Chemotherapy. I. The Trypanocidal Action of Antimony Compounds.** CARL VOEGTLIN and HOMER W. SMITH [with MARIAN M. CRANE, KATHERINE D. WRIGHT, and MABEL A. CONNELL] (*J. Pharm. Exp. Ther.*, 1920, **15**, 453—473).—The specific action of antimony lactate can be studied fairly accurately by following the disappearance of the trypanosomes from the blood stream of infected rats. There is a sharply defined threshold stage, below which the drug has no appreciable effect on the parasites. The process curve is an orderly one, and consistent throughout individual experiments.

J. C. D.

**Quantitative Studies in Chemotherapy. II. The Trypanocidal Action of Arsenic Compounds.** CARL VOEGTLIN and HOMER W. SMITH [with MARIAN M. CRANE, KATHERINE D. WRIGHT, and MABEL A. CONNELL] (*J. Pharm. Exp. Ther.*, 1920, **15**, 475—493).—Differences in the toxicity of various arsenic preparations have been explained on the hypothesis that they must be changed into one type, namely, the trivalent oxides,  $RAs_2O$ , before exerting their principal toxic effect. J. C. D.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Metabolic Action of Bacteria.** FRITZ VERZÁR and JOSEF BÖGEL (*Biochem. Zeitsch.*, 1920, **108**, 207—219).—*Streptococcus haemolyticus* forms only acid, but not alkali, with dextrose. The acidity attained by *Bacillus paratyphosus*-B and *B. proteus* is independent of the initial reaction. In the formation of acid, *B. coli communis* produces gas; on the other hand, it uses up oxygen when it forms alkali. There is no connexion between mobility and gas formation in paratyphoid organisms. Ethyl alcohol, methyl alcohol, chloroform, and formaldehyde inhibit the gas exchange of these organisms. Much smaller doses produce definite retardation. A relation between the maximum acid formation and the presence of alcohols is established. S. S. Z.

**The Chemical Composition of the Tubercle Bacillus.** A. GORIS (*Ann. Inst. Pasteur*, 1920, **34**, 497—546).—See this vol., i, 582.

**Antagonistic Action of Calcium and Iron Salts toward other Salts as measured by Ammonification and Nitrification.** J. E. GREAVES (*Soil Sci.*, 1920, **10**, 77—102).—Experiments were made on the effect produced on the bacterial activity of a fertile, sandy loam soil by the addition of calcium and iron salts. The ammonifying and nitrifying powers of the soil were first reduced by the addition of various salts, then increasing amounts of the calcium salt or the iron salt were added, and the effect on ammonification and nitrification was observed. Calcium sulphate was found to neutralise the toxic effect on ammonification of sodium carbonate, nitrate, and sulphate, calcium chloride, and magnesium chloride and sulphate. It had no antagonism to sodium chloride. Similar results were obtained in the case of nitrification, except that there was no antagonism towards sodium sulphate and calcium chloride. Thus both the anion and cation take part in the antagonism.

Ferrous sulphate was found to be antagonistic to sodium sulphate, chloride, carbonate and nitrate, and calcium chloride; ferrous chloride to sodium chloride and nitrate, calcium chloride, and magnesium sulphate; ferrous nitrate to magnesium chloride and sulphate, calcium chloride, and sodium carbonate, sulphate, chloride, and nitrate; ferrous carbonate to sodium chloride and carbonate, calcium chloride, and magnesium sulphate. The greatest effect was produced by ferrous carbonate on magnesium sulphate, in which mixture 75% of the toxic effect was neutralised. In the case of nitrification, the order differed, and the greatest effect was produced by ferrous nitrate against magnesium chloride. The quantity of iron required for maximum effect varied with the different salts, but in no case exceeded 186 parts per million.

J. H. J.

**The Pharmacology of Selenium and Tellurium. I. The Action of their Acids on Bacteria.** GEORG JOACHIMOGLU (*Biochem. Zeitsch.*, 1920, **107**, 300—312).—The ions of tellurous and selenious acids are much more active than those of telluric and selenic acids. The growth of moulds is scarcely affected by the action of tellurites and tellurates. Bacteria, especially of the typhus-coli group, are, on the other hand, very sensitive to the action of these substances. The author suggests the application of tellurium compounds in the chemotherapy of typhoid infection.

S. S. Z.

**Oligodynamy of Silver.** R. DOERR (*Biochem. Zeitsch.*, 1920, **106**, 110—133).—"Oligodynamic" water, that is, water which by prolonged contact with metallic silver has become bactericidal, shows all the properties of an antiseptic. Dilution with distilled water or concentration by distillation produces the corresponding

quantitative change, but no qualitative change, in the antiseptic power; the distillate acquires no such property. If reducing substances are excluded, boiling causes no diminution in the bactericidal action of the water. The presence of sodium chloride retards this action, and that of horse serum destroys it. The antiseptic property of oligodynamic water appears to be to some extent specific, bacteria of different species exhibiting resistance in different degrees. Solutions of definite silver compounds show the same properties as oligodynamic water.

T. H. P.

**Oligodynamics of Silver. II.** R. DOERR (*Biochem. Zeitsch.*, 1920, **107**, 207—218).—The bactericidal action of metallic silver disappears when the metal is ignited, boiled several times in distilled water, or is embedded in an agar jelly. The inactivated metal can be reactivated by being treated with very dilute solutions of a strongly dissociated acid. The oligodynamic principle of silver is dialysable, and shows the same properties of diffusion in agar jellies as silver oxide and silver nitrate. Bacteria seeded on an agar plate containing metallic silver, silver oxide, or silver nitrate grow often in two concentric rings similar to the Liesegang phenomenon. Pieces of silver embedded in a blood-agar plate produce hæmolytic zones.

S. S. Z.

**The Antiseptic Action of Some Chlorine Derivatives of Methane, Ethane, and Ethylene.** E. SALKOWSKI (*Biochem. Zeitsch.*, 1920, **107**, 191—201).—The suitability as preservatives of methyl chloride, chloroform, methylene chloride, acetylene dichloride, trichloroethylene, and ethyl chloride was tested. Trichloroethylene, on account of its low price, of the small quantities required to be employed, and of its volatile character, was found to be the most suitable preparation.

S. S. Z.

**Dependence of Yeast-growth and Fermentation on Physico-chemical Phenomena.** FRIEDRICH BOAS (*Biochem. Zeitsch.*, 1920, **105**, 193—198).—The author's experiments on the fermentation of dextrose solutions containing different proportions of ammonium sulphate confirm the observation that fermentation exhibits an optimum for a definite concentration of nitrogenous material. The results obtained by Pringsheim (A., 1907, ii, 287; 1908, ii, 316) with asparagine and ammonium sulphate are considered in the light of colloidal chemistry; and the conclusion is drawn that the plasma membrane of the yeast cell, somewhat in the same way as a lecithin membrane, is rendered either denser or looser by different concentrations of nitrogenous substances, the sugar thus entering the yeast cell either slowly or rapidly, and the fermentation being correspondingly slow or rapid. When peptone is used as source of nitrogen, maxima of fermentation similar to those obtained with asparagine, etc., are observed at first, the peptone being thus converted into crystalloid nitrogen compounds at the plasma membrane; this phenomenon soon disappears, owing, presumably, to the formation from the peptone of compounds which

counteract the crystalloid compounds. These membrane effects are observed also with synthetic leucine, but not with natural leucine derived from molasses.

T. H. P.

**Rhythmic Phenomena in the Growth and Fermentation of Yeast.** ERICH KÖHLER (*Biochem. Zeitsch.*, 1920, 106, 194—206).—The processes of fermentation and of multiplication of yeast are found to exhibit a certain periodicity, which is caused by alterations in the sugar and alcohol contents of the nutrient solution. The velocity with which the yeast grows is conditioned by the concentration of the sugar, and varies irregularly as this concentration increases.

T. H. P.

**Course of Alcoholic Fermentation by Yeast.** ERICH KÖHLER (*Biochem. Zeitsch.*, 1920, 108, 235—243).—The course of alcoholic fermentation by yeast becomes rhythmic with the increase in the concentration of the alcohol.

S. S. Z.

**Formation of Acid with Moulds and Yeasts. IV.** FRIEDRICH BOAS, HANS LANGKAMMERER, and HANS LEBERLE (*Biochem. Zeitsch.*, 1920, 105, 199—219. Compare A., 1919, i, 508).—The results of further experiments with yeasts indicate that different sugars act to different extents on the plasmic membrane, so that they may be arranged in order of diminishing utilisability by yeasts, as follows: maltose, dextrose, lævulose, sucrose. With many yeasts, this action on the membrane is zero with maltose and very considerable with sucrose. Such specific action of the sugars may be more or less altered, but not obliterated, by acclimatisation. Further, from the results obtained by other investigators, it appears that alteration in the reaction of the liquid and in the concentration of the nitrogenous substances may effect slight displacements in the above series of sugars. With a maltose solution containing ammonium chloride, the maximal acidity reached during fermentation was  $p_H=2.55$ , and with a whortleberry juice containing sucrose and ammonium chloride, the value  $p_H=1.85$  was reached on brisk fermentation (compare Euler and Heintze, this vol., i, 513).

T. H. P.

**Maltase Solutions from Yeast.** R. WILLSTÄTTER, TR. OPPENHEIMER, and W. STEIBELT (*Zeitsch. physiol. Chem.*, 1920, 110, 232—240).—Maltase can be obtained from fresh beer yeast previously killed by an antiseptic, such as chloroform or toluene, by extracting it with water in the presence of ammonia. The authors suggest that, owing to some enzymic process, acid is formed in the yeast cell, which is responsible for the destruction of the maltase when it is extracted from the undried cell, and that the neutralising effect of the ammonia makes it therefore possible to obtain the enzyme also from the fresh yeast cell. The relation between the concentration of the enzyme and the decomposition of the maltose, as well as the velocity of the reaction, was studied

with maltase preparations from dried and fresh yeasts. The activity of maltase solutions is impaired by treatment with kaolin.  
S. S. Z.

**The Influence of Surface-active Nonoic Acid and of Some Surface Active Homologues of the Alcohol Series (Amyl Alcohol and Octyl Alcohol) on the Yeast Cell and on Fermentation.** WILHELM WINDISCH, WILHELM HENNEBERG, and WALTHER DIETRICH (*Biochem. Zeitsch.*, 1920, **107**, 172—190).—0.005—0.02% of nonoic acid has an inhibitive action on yeast fermentation. 0.017—0.04% of octyl alcohol has a similar effect. Higher concentrations of amyl alcohol are required to produce inhibition in fermentation. Nonoic acid and octyl alcohol also produce a diseased condition of the yeast cell, altering its appearance with the production of fat in the cell. The experiments point to the fact that the action of these substances is not due to their chemical properties, but to their surface action. S. S. Z.

**Physico-chemical Considerations in connexion with Neuberg's Theory of Fermentation.** WOLFGANG OSTWALD (*Biochem. Zeitsch.*, 1919, **100**, 279—288); CARL NEUBERG (*ibid.*, 289—303).—A suggestion is put forward by Ostwald that physical factors, such as adsorption, might exercise some influence in the fixation of intermediate products of fermentation, such as acet-aldehyde. To this Neuberg replies. S. S. Z.

**The Relation of Aldehydes to Alcoholic Fermentation.** CARL NEUBERG and MARTA EHRLICH (*Biochem. Zeitsch.*, 1920, **101**, 239—277. Compare A., 1918, i, 469).—The influence of seventy-one aldehydes on alcoholic fermentation was tested. It was found that the stimulating effect of the aldehyde group was general and independent of the radicle associated with it. This activation takes place whether the fermentation is produced by the living yeast or by the cell-free juice. S. S. Z.

**The Relation of Phytochemically Reducible Substances to the Process of Alcoholic Fermentation and the Nature of the Action of Activators.** CARL NEUBERG and MARTA EHRLICH (*Biochem. Zeitsch.*, 1920, **101**, 276—318. Compare preceding abstract).—Numerous experiments are described which show that most ketones and their derivatives and phytochemically reducible substances are capable of activating alcoholic fermentation. This activating influence is not so marked, in fact, almost absent, with the lower ketones. S. S. Z.

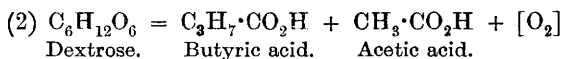
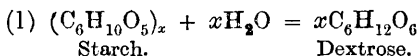
**So-called Methyl-alcoholic Fermentation.** EDMUND O. VON LIPPMANN (*Biochem. Zeitsch.*, 1920, **106**, 236—238).—Examination of twenty samples of genuine rums confirms the observation that such spirits often contain methyl alcohol in considerable proportion, as much as 7.5—8.5% of this alcohol being found in three of the samples. Much of the extraction of sugar

cane in the Lesser Antilles is carried out in presses, and the juice is subjected to inadequate clarification and mechanical purification, so that it contains considerable proportions of very fine cane fibre, which passes to a large extent into the syrups and molasses. This fibre is rich in pectinous material, and as the pectins consist of the methyl ester of pectinic acid and are readily decomposed in various ways, with liberation of methyl alcohol, the origin of the latter is evident.

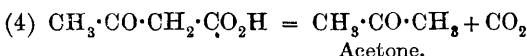
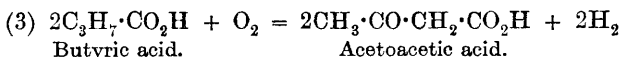
T. H. P.

**Production of Gas during the Acetone and Butyl Alcohol Fermentation of Starch.** HORACE B. SPEAKMAN (*J. Biol. Chem.*, 1920, **43**, 401—411).—From a study of the production of gas during this fermentation, a scheme is suggested to account for the substances formed which is believed to be in harmony with experimental observations, the requirements of the organism, and the conditions during fermentation.

It has been previously shown that the first two stages of the fermentation may be represented by the equations

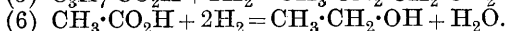
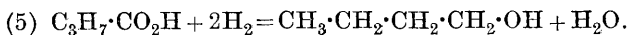


The oxygen produced during the second reaction cannot be detected by ordinary chemical methods, and must therefore be used up in associated reactions, in which oxidation plays a part. Now, production of acetone commences very early in the fermentation and before the appearance of the butyl alcohol, whilst the gas given off at the commencement is pure hydrogen, but later a gradual and increasing dilution with carbon dioxide occurs. From this evidence it may be concluded that a later stage of the fermentation may be represented by the equations:



The intermediate formation of acetoacetic acid has not been proved experimentally, but Raistrick and Clark (this vol., i, 352) have already suggested that it occurs.

The formation of butyl alcohol, and to a much smaller degree of ethyl alcohol, takes place by the reduction of the corresponding acid:



Other points require further study, as, for example, the disappearance of a larger amount of acetic acid than can be accounted for by the amount of ethyl alcohol produced, the volume of



hydrogen and carbon dioxide given off, which cannot be accounted for by the activity of reactions previously mentioned in this scheme, and the consumption of oxygen made available by the production of butyric acid, which is not oxidised to acetone, but reduced to alcohol.

J. C. D.

**The Third Form of Fermentation of Sugar.** CARL NEUBERG and JULIUS HIRSCH (*Biochem. Zeitsch.*, 1919, **100**, 304—322).—In the presence of alkaline salts, sugar, when fermented by yeast, undergoes a cleavage into acetic acid, ethyl alcohol, carbon dioxide, and glycerol. This abnormal fermentation the authors call the "third form of fermentation," in contradistinction to the normal process and the process of fermentation carried out by fixing the acetaldehyde produced with an agent, such as sodium sulphite—"the second form of fermentation." Fermentation of sugar by yeast in the presence of potassium carbonate, dipotassium phosphate, magnesium oxide, trisodium phosphate, disodium phosphate, and a "buffer mixture" of monosodium and disodium phosphate, yielded products of fermentation characteristic of the "third form of fermentation." In the presence of aluminium hydroxide and colloidal iron hydroxide, the fermentation was normal. During fermentation of sugar in molar dipotassium phosphate, a sixfold production of acetaldehyde is observed in the early stages of the fermentation. This falls to the normal rate as fermentation proceeds.

S. S. Z.

**The Gaseous Exchanges of the Root with the Atmosphere.** RAOUL CENGHELLI (*Compt. rend.*, 1920, **171**, 575—578).—In a confined atmosphere, plant roots respire in much the same way as other organs, the ratio of carbon dioxide expired to oxygen inspired varying from 0.7 to 1, according to the species. In a very moist atmosphere there is an increase in the rate of respiration, but the above ratio remains constant. When the roots are in contact with a very moist atmosphere and still attached to the aerial organs, there is further increase in the respiration, but the carbon dioxide formed is not completely expired, so that the respiratory-coefficient is low.

W. G.

**The Velocity of the Photochemical Degradation of Carbon Dioxide in Living Cells.** OTTO WARBURG (*Biochem. Zeitsch.*, 1919, **100**, 230—270. Compare this vol., i, 583).—The velocity of assimilation of carbon dioxide is proportional to the concentration of the gas when the concentration is low. With higher concentrations, the velocity of assimilation increases proportionately less as the concentration of the carbon dioxide increases until it is no more influenced by the concentration. In the case of illuminations of low intensity, the velocity of assimilation is also proportional to the intensity of the illumination, but with higher illuminations the increase in the velocity of assimilation becomes lower as the intensity of the illumination increases.

Temperature influences the assimilation of carbon dioxide in high concentrations of the gas when intensely illuminated in a pronounced degree. Between  $5^{\circ}$  and  $32^{\circ}$ , the temperature-coefficient sinks from 4.3 to 1.6. In the case of illuminations of high intensity, more carbon dioxide is decomposed by the same quantity of energy when the illumination is intermittent than when it is continuous. This differentiation does not take place when the illumination is low. The influence of phenylurethane and of hydrocyanic acid on the carbon dioxide assimilation and on the respiration of algæ was also studied. S. S. Z.

**Adsorption and Modification of Food Materials by Plants.** E. REINAU (*Zeitsch. Elektrochem.*, 1920, 26, 329—342). Corresponding with the theory of the assimilation of carbon dioxide by plants, a similar hypothesis is proposed for the other elementary food materials, and conclusions are drawn therefrom for the complete metabolism of plants; the idea of physiological concentration receives an explanation thereby. The different stages passed through by the elementary food materials are somewhat as follows: acceptor compound, assimilation substances of varying complexity, acceptor substance, acceptogen, structure material and reserve matter, degradation products. The natural periodic sequence in the formation of these different substances necessitates a continuously varying provision of the corresponding elementary food materials to the plant. To secure the highest cultural result, therefore, the metabolism for each specific element must be separately considered. The various individual metabolisms are, however, inseparably connected since the elementary food materials, singly or in conjunction, may in the form of acceptor substance chemically or physically attract another elementary food material. The hydrostatic osmotic action of carbon metabolism towards water in plants is considered, and from this point of view the connexion between the phenomena of the nutrient salt economics of plants and the height of their growth is explained. In the light of the author's theory, a simple explanation of the relationship between the increase of a vegetation factor and the mass production of plants is given. Certain peculiar phenomena observed in the carbon-dioxide manuring of plants are brought into the general scheme of metabolism.

Certain analogies to the principles of material metabolism in plants are shown when changes of energy are considered.

All the conceptions thus developed depend on the lytic properties of water and the associations and dissociations which occur within the individual cell surrounded by walls of varying permeability.

It is further shown that the elementary food materials consist of substances of low atomic or molecular weight, that the continuously increasing condensation and formation of insoluble products direct the stream of nutrient material in a definite direction, and that this action is supplemented by the behaviour of the condensation products at the differently permeable cell walls whereby the backward flow of the elementary substances is hindered. H. W.

**Formaldehyde as an Intermediate Stage between the Real Assimilation and the Formation of Carbohydrates in Plants.** MARTIN JACOBY (*Biochem. Zeitsch.*, 1919, 101, 1—6).—Leaves of *Tropaeolum majus* were exposed to formaldehyde in the dark, and it was found that an increase in the dry matter took place in these leaves as compared with control leaves when certain conditions were observed. The author considers that the formaldehyde was not fixed, but actually transformed into tissue of the plant. S. S. Z.

**Selective Absorption of Ions from Equilibrated Solutions.** E. PANTANELLI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1920, 26, 136—151).—Experiments have been made on the absorption of the different ions in salt solutions by marine algæ and by terrestrial plants. T. H. P.

**Distribution of Lycorine in the N.O. Amaryllidaceæ. II.** K. GORTER (*Bull. Jard. bot. Buitenzorg*, 1920, [iii], 2, 331—334. Compare this vol., i, 467).—The crystallised alkaloid has been isolated from the bulbs and roots of *Amaryllis Belladonna*, L., *Clivia miniata*, Benth., *Cooperia Drummondii*, Herb., *Cyrtanthus pallidus*, Sims, and *Sprekelia formosissima*, Herb. (yield, 0.1—0.01% and less). It is doubtless identical with “belamarine” from the first-named species and with “amarylline” from the last-named, both isolated by Fragner (A., 1891, 1122), and also with the veratrine-like alkaloid obtained by Molle from the second species (*Jahresb. Pharm.*, 1903, 27). G. B.

**Constituents of Digitalis.** WILLIAM J. MCGILL (*J. Amer. Chem. Soc.*, 1920, 42, 1893—1900).—By careful manipulation and uniform methods of procedure, using various solvents, it is possible to obtain crude fractions from digitalis which will have a reasonably constant chemical composition. The cold water extract of the leaves contains either none or a very minute quantity of digitoxin, its activity being entirely due to two fractions, soluble and insoluble in chloroform respectively (compare Kraft, A., 1912, i, 373). The digitsaponin of digitalis leaves is found to be totally inactive and non-hæmolytic when purified. The chloroform-soluble fraction obtained by Hatcher (compare *J. Amer. Pharm. Assoc.*, 1919, 8, 913) from the hot water extract of the leaves is a mixture of gitalin and digitoxin. W. G.

**The Appearance and the Emulsifying Action of Various Substances in the Cells of the Leaves of *Fontinalis antipyretica*.** KARL BORESCH (*Biochem. Zeitsch.*, 1919, 101, 110—158).—The fatty nature of the thread-like convolutions present in the cells of the leaves of *Fontinalis antipyretica* has been established by means of microchemical methods. Alcohols, phenols, alkaloids and their salts, ammonia and its salts and its derivatives, produce the disintegration of these convolutions into small drops (emulsification). The emulsifying action of substances belonging to the groups mentioned has been studied in detail. S. S. Z.

**"Taifushi" Oil.** S. KEIMATSU (*J. Pharm. Soc. Japan*, 1920, 283—296).—"Taifushi" oil, m. p. 22—23°,  $D_{15}^{20} 0.952$ ,  $[\alpha]_D^{20} +51.2^\circ$ , acid number 12.06, saponification number 20.30, iodine number 85.05, is the oleum gynocardiae (oleum chaulmoogræ) of the Japanese pharmacopœia, but, in the author's opinion, is obtained from neither *Gynocardia odorata*, R. Br., nor *Taraktogenos kurzii*, King, but from the seeds of *Hydnocarpus anthelmintica*, Pierre. It contains palmitin, but its chief constituents are glyceryl chaulmoograte and hydnocarpate. A dihydroxyhydnocarpic acid,  $C_{15}H_{27}(OH)_2 \cdot CO_2H$ , m. p. 83°, is obtained by oxidising hydnocarpic acid at a low temperature.

CHEMICAL ABSTRACTS.

**Phytin. XVI. Occurrence of Inositolhexaphosphoric Acid in the Seed of the Silver Maple (*Acer Saccharinum*).** R. J. ANDERSON [with W. L. KULP] (*J. Biol. Chem.*, 1920, 43, 469—475).—From the freshly powdered maple seed, a crystalline barium salt corresponding with tribarium inositolhexaphosphate was isolated. The freshly powdered seed does not, apparently, contain any active phytase. The examination of a sample of seed which had been stored for some time showed that some hydrolysis of the organic phosphorus compounds had occurred, for the salt isolated was apparently a barium salt of inositolpentaphosphoric acid.

J. C. D.

**The Biochemical Method of Detection of Glucosides Hydrolysable by Emulsin.** EM. BOURQUELOT (*Compt. rend.*, 1920, 171, 423—425. Compare Delauney, succeeding abstract).—A brief review of the work accomplished by this method. W. G.

**Extraction of Glucosides from Two Indigenous Orchids; Identification of these Glucosides with Loroglossin.** P. DELAUNEY (*Compt. rend.*, 1920, 171, 435—437).—The author has isolated from *Orchis Simia*, Lam., and *Ophrys aranifera*, Huds., a crystalline glucoside identical in each case with the loroglossin obtained from *Loroglossum hircinum*, Ric., by Bourquelot and Bridel (A., 1919, i, 243).

W. G.

**The Action of Pectase.** HANS VON EULER and OLOF SVANBERG (*Biochem. Zeitsch.*, 1919, 100, 271—278).—The coagulation of the juice of *Ribes nigrum* is not due to any change in the hydrogen-ion concentration, but is brought about by the action of an enzyme. When the juice is heated at 95° or 75° for five minutes, no coagulation takes place after three days. The optimum H-ion concentration for the activity of the enzyme is  $p_H=4.3$ . The pectase of *R. rubrum* coagulates the pectin of *R. nigrum*.

S. S. Z.

**The Formation of Melanin in Autolysed Potato Juice.** HUGO HAEHN (*Biochem. Zeitsch.*, 1919, 100, 114—129).—The dark coloration of potato juice is due to the formation of melanin by tyrosinase from the tyrosine of the juice. The "melanin value" is the number of c.c. of 0.002*N*-potassium permanganate necessary to decolorise 1 c.c. of boiled and filtered juice. During storage of potato juice at 37°, the proteins in it are autolysed and more tyrosine is set free, which is responsible for a higher "melanin

value." The difference in the "melanin value" before and after autolysis—"the autolytic value"—varies with the different varieties of potatoes. Six months' storage of the potato tuber produces an increase in the amino-acids, but a decrease in the tyrosinase. The formation of melanin is increased in weakly alkaline solution when the juice is stored in a warm place. S. S. Z.

**Investigation of *Plantago coronopus*, L.** EM. EMMANUEL and M. PAPAVALION (*Arch. Pharm.*, 1920, **258**, 142—147).—The plant is indigenous to Greece and the surrounding countries; preparations of it are used as powerful diuretics.

The seeds yield 44.2% of mucus and 4.6% of a gum which is soluble in water, shows the reactions of the pentoses, and is converted by nitric acid into mucic acid.

The whole plant, excluding the seeds, was exhaustively extracted with alcohol (95%); the concentrated extract deposited small quantities of chlorophyll and sodium chloride. The filtrate was diluted with water containing sulphurous acid, and the precipitate formed separated by ether into insoluble *plantagenic acid*,  $C_9H_{12}O_2$ , m. p.  $210^\circ$  (the *silver salt* was analysed), and soluble resin, acid number 73.39, saponification number 158.7, from which sodium hydroxide solution extracted *coronopic acid*,  $C_{54}H_{66}O_2$ , amorphous, white mass, m. p.  $281$ — $282^\circ$ , whilst from the portion left after this treatment a pale yellow, mobile essential oil,  $n_D^{40}$  1.6893, was obtained in very small amount by distillation with steam, the remainder consisting of a *resin*, m. p.  $128$ — $130^\circ$ , which evolved benzoic acid when heated on platinum foil. The presence of bitter principles or glucosides could not be detected, but emulsin and invertin were found by Bourdier's method.

The plant yields 7% of ash containing aluminium, magnesium, sodium, potassium, silica, chlorine, phosphoric and sulphuric acids; the presence of lithium could not be detected spectroscopically. The diuretic action of the plant, which has frequently been attributed to the latter element, is probably due to its high content in mucus. H. W.

**The Ragweed Pollen Proteins.** FREDERICK W. HEYL and HARRIS H. HOPKINS (*J. Amer. Chem. Soc.*, 1920, **42**, 1738—1743. Compare Heyl, A., 1919, i, 373).—The proteoses, the albumin, and the glutelin from ragweed pollen have been hydrolysed with 20% hydrochloric acid, and the various amino-acids, etc., estimated in the product by the Van Slyke process. Histidine is entirely absent from the proteoses and albumin. W. G.

**Some Constituents of *Viburnum prunifolium*.** FREDERICK W. HEYL and CHARLES BARKENBUS (*J. Amer. Chem. Soc.*, 1920, **42**, 1744—1755).—The dried root bark of *Viburnum prunifolium* was examined by the usual methods. Amongst the various products were acetic and valeric acids in the free state, as complex esters soluble in water and as resinous esters insoluble in water. The resin insoluble in water contained a new *phytosterol*, m. p.  $186$ — $187^\circ$ ,  $[\alpha]_D +115^\circ$  (in chloroform), giving an *acetate*, m. p.  $223$ — $224^\circ$ . The fat from this resin contained formic, acetic, hexoic, octoic, myristic, palmitic, oleic, and linolic acids, but no

valeric acid. A trace of an amorphous alkaloid was found in the alcoholic extract. W. G.

**Certain Physiological Actions of Osmium Tetroxide.** RUD. SEELIGER (*Ber. Deut. bot. Ges.*, 1920, **38**, 176—184).—The wheat corn withstands for some hours, without being killed, relatively high concentrations of osmium tetroxide, although in lower concentrations this oxide retards germination, delays growth, and results in diminution of the magnitude of the organs of the young plant. The parenchymatous cells of the red beet are highly sensitive to the action of osmium tetroxide. T. H. P.

**Ripening of Cereals.** HEINRICH LÜERS (*Biochem. Zeitsch.* 1920, **104**, 30—81).—A new method is described of estimating acidity in organic extracts, the acid being titrated against both neutral-red and phenolphthalein in one and the same test liquid; this method gives reproducible results. An improvement is introduced into Sørensen's formol-titration method, the end-point being determined, not by means of azolitmin paper, but by titration in presence of neutral-red.

These two methods have been applied to follow the alterations in acidity, formol-titratable nitrogen, and enzymic relations of barley, wheat, oats, and rye during the last stages of ripening and subsequent storage for two months. The first two magnitudes diminish during the ripening, and, to a less extent, during storage, the acid passing into organic combination and the formol-titratable substances undergoing condensation to more highly complex compounds. In most cases the enzymic properties become more marked as ripening proceeds, but in some instances a diminution, followed by an increase, occurs; the enzymic changes taking place in the ripening and resting corn are considered from different chemical, physical, and colloid-chemical points of view. T. H. P.

**Effect of various Soluble Salts and Lime on Evaporation, Capillary Rise, and Distribution of Water in some Agricultural Soils.** M. I. WOLKOFF (*Soil Sci.*, 1920, **9**, 409—436).—The salts used were ammonium, potassium, and magnesium sulphates, sodium chloride, calcium nitrate, potassium phosphate, and calcium oxide, these being applied at the rate of approximately 2510 kilos. per hectare to different types of soil. The results obtained varied considerably with the particular salt used and the soil to which it was applied. In general, soluble salts materially decrease the evaporation of soil moisture, there being apparently a direct relationship between the efficiency of the salts in this respect and the osmotic concentration of the soil solution in the surface 2.5 cm. of soil. The greater this osmotic concentration, the greater is the depression of the evaporation. Of the salts studied, sodium chloride and calcium nitrate were most effective and potassium sulphate and phosphate least effective in checking the evaporation. In this respect calcium oxide was least effective in sea sand and sandy loam and most effective in clay loam.

In two of the soils sodium chloride decreased the capillary rise, whilst calcium oxide in drab clay and potassium phosphate in a silt

loam tended to increase the rise, ammonium sulphate showing no pronounced effect.

In soils treated with sodium chloride, potassium phosphate or calcium oxide there was a pronounced tendency for an increase in the water content of the top 20 cm., and soil treated with potassium phosphate or calcium oxide contained more water even in the top inch than the untreated soil, although evaporation was decreased from the treated soil.

W. G.

**Distribution of Titanium in Soils and Plants.** GEILMANN (*J. Landw.*, 1920, **68**, 107—124).—The estimation of titanium dioxide in soils may be carried out by a modification of Hillebrand's method ("Analysis of Silicate and Carbonate Rocks," see this vol., ii, 449). Titanium dioxide is widespread in soils in proportions varying from traces to 1%, the content generally lying between 0.3% and 0.6%. Of a number of plants examined, nearly all contain titanium, which occurs in largest proportion in the green parts of the plants. Plant ashes contain from traces to 0.27% of  $\text{TiO}_2$ .

T. H. P.

**Acid Clay and Acid Soil.** KIUHEI KOBAYASHI (*J. Chem. Ind Japan*, 1920, **23**, 549—555).—Reviewing theories on the acidity of soil, the author attributes the acidity to the adsorptive properties of Japanese acid clay or like substances mixed with it. (Compare this vol., i, 704).

K. K.

**The Importance of Liming Soils containing Humus.** SVEN ODÉN (*Internat. Mitt. Bodenkunde*, **9**, 375—390; from *Chem. Zentr.*, 1920, iii, 396).—The favourable influence of lime on soils containing humus depends primarily on the formation of utilisable calcium humates. In this manner, toxic acids are neutralised, and formation of acid is hindered by the calcium humate. In addition, the calcium salts displace adsorbed nutrient matter, thus rendering it available for the plant. A marked effect on irrigation is not observed, but the oxidative capacity of the humic salts is a powerful factor.

H. W.

**Acidity of Mineral Acid Soils.** S. OSUGI and T. UETSUKI (*Ber. Ohara Inst. landw. Forsch.*, 1916, **1**, 27—52; from *Chem. Zentr.*, 1920, iii, 395—396).—When the bases of the soil are rapidly diminished by marked weathering, colloidal substances are formed which adsorb the bases; free acids are obtained when such soils are treated with solutions of salts. Since the soil contains alumina and other compounds, which are readily decomposed by hydrochloric acid, but not by acetic acid, the filtrates from soils which have been treated with the former are rich in aluminium, whilst those obtained when potassium acetate is used contain but little of this metal. The differing intensities of the acidities of the filtrates thus obtained depend, in the first place, on the acid which has been liberated by the adsorption process in the soil. An acid soil must therefore be regarded as one which is incompletely saturated with bases.

H. W.

## Organic Chemistry.

**Behaviour of Methane at High Temperatures Alone and in Contact with the other Constituents in Firedamp Explosions.**

H. WINTER (*Brennstoff-Chem.*, 1920, **1**, 17—22).—In mixtures of pure methane and air containing from 5.0 to 9.2% of methane, the combustion occurs according to the equation  $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$ . In mixtures containing 9.2 to 14% of methane, the combustion of the methane is incomplete. In addition to carbon dioxide, water, and hydrogen, the residues contain carbon monoxide when the ratio of oxygen to methane is somewhat greater than, equal to, or less than,  $\text{O}_2:\text{CH}_4 = 2.0$ . When the concentration of oxygen becomes smaller, hydrogen appears in addition to carbon dioxide and monoxide, nitrogen and water. The explosion under these conditions is also accompanied by deposition of carbon within a small area.

J. R. P.

**The Dehydrogenation of Alcohols by Catalytic Oxidation under Reduced Pressure.**

CHARLES MOUREU and GEORGES MIGNONAC (*Compt. rend.*, 1920, **171**, 652).—The method previously described (this vol., i, 283) is modified so that the alcohol vapour and oxygen are passed, at a reduced pressure of 20—40 mm., over the catalyst, finely divided silver, at 230—300°. Under these conditions, satisfactory results are obtained with the higher alcohols.

W. G.

**The Reaction between Alcohols and Aqueous Solutions of Hydrochloric and Hydrobromic Acids. II.**

JAMES F. NORRIS and ROBERT S. MULLIKEN (*J. Amer. Chem. Soc.*, 1920, **42**, 2093—2098).—In continuation of previous work (A., 1916, i, 461), it is shown that aqueous hydrobromic acid reacts with certain di- and tri-hydroxy-alcohols and certain cyclic alcohols. Hydrochloric acid replaced the hydroxyl group in certain of the alcohols containing negative substituents, but its failure to act in other cases indicated that influences other than those of negative groups serve to activate the hydroxyl group.

W. G.

**Chloromethyl Carbonates: Systematic Chlorination of Methyl Carbonate.**

ANDRÉ KLING, D. FLORENTIN, and E. JACOB (*Ann. Chim.*, 1920, [ix], **14**, 189—214).—A more detailed account of work already published (this vol., i, 213).

W. G.

**New Syntheses of  $\alpha$ -Monoglycerides.** EMIL FISCHER, MAX BERGMANN, and HEINRICH BÄRWIND (*Ber.*, 1920, **53**, [B], 1589—1605).—The general methods for the preparation of mono- and di-glycerides depend either on the action of glyceryl chlorohydrins on the salts of fatty acids or on esterification of the fatty acid with the chlorohydrin, and subsequent exchange of the halogen atoms for the hydroxyl group. Neither process is suitable



for synthetic operations, since the former method is complicated by side reactions, and no guarantee is afforded of the simple replacement of the halogen atom by the fatty radicle (compare Fischer, Bergmann, and Lipschitz, A., 1918, i, 172), whilst in the latter the halogen atom can, in general, be only replaced under conditions which readily occasion further change. As initial material in a new series of syntheses, the authors have therefore adopted "acetone glycerol," which has been shown by Irvine, Macdonald, and Soutar (T., 1915, 107, 337) to be isopropylidene-

glycerol,  $\text{CMe}_2 \begin{smallmatrix} \text{O} \cdot \text{CH}_2 \\ | \\ \text{O} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OH} \end{smallmatrix}$ ; this substance reacts readily with acid chlorides in the presence of quinoline, yielding products, from which the acetone residue is readily removed by mild treatment, thus giving undoubted  $\alpha$ -monoglycerides.

*Benzoylisopropylideneglycerol*,  $\text{CMe}_2 \begin{smallmatrix} \text{O} \cdot \text{CH}_2 \\ | \\ \text{O} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OBz}' \end{smallmatrix}$  large, monoclinic crystals,  $a:b:c=1.0221:1:0.4661$ ,  $\beta=108^\circ 56'$ , m. p.  $34.5^\circ$ , b. p.  $164\text{--}165^\circ/9\text{--}10$  mm., is readily obtained by the action of benzoyl chloride on an ice-cold mixture of isopropylidene-glycerol and quinoline, and is transformed by  $N/2$ -hydrochloric acid at  $55\text{--}60^\circ$  into  $\alpha$ -monobenzoylglycerol, m. p.  $36^\circ$  (compare Krafft, A., 1904, i, 136), which is partly decomposed on distillation, even in a high vacuum, into glycerol and dibenzoylglycerol; it re-forms the isopropylidene compound in good yield when treated with dry acetone containing 1% of hydrogen chloride, and with phenylcarbimide gives the corresponding diphenylurethane, small needles arranged in clusters, m. p.  $135\text{--}136^\circ$  (corr.). *p*-Nitrobenzoylisopropylideneglycerol, leaflets, m. p.  $56^\circ$ , and  $\alpha$ -*p*-nitrobenzoylglycerol, pale yellow prisms, m. p.  $107^\circ$ , are similarly prepared; the latter is converted by benzoyl chloride in the presence of chloroform and pyridine into  $\beta\gamma$ -dibenzoyl- $\alpha$ -*p*-nitrobenzoylglycerol,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}(\text{OBz}) \cdot \text{CH}_2 \cdot \text{OBz}$ , colourless, four-sided needles, m. p.  $114^\circ$  (corr.).

Stearyl chloride, b. p.  $164\text{--}166^\circ/0.5\text{--}1$  mm., transforms isopropylideneglycerol into stearyl isopropylideneglycerol, long, colourless needles, m. p.  $40\text{--}41^\circ$  after slight softening at  $37^\circ$ , which is converted by aqueous hydrochloric acid in the presence of ether into  $\alpha$ -monostearin, which generally has m. p.  $81\text{--}82^\circ$ ; a second modification, m. p.  $75\text{--}76^\circ$ , is obtained when the first form is melted and allowed to solidify or rapidly crystallised from ether. *Laurylisopropylideneglycerol*, pale yellow, mobile oil, has b. p.  $151\text{--}152^\circ/0.2\text{--}0.3$  mm., m. p.  $+8\text{--}9^\circ$ ,  $D_4^{25} 0.9537$ ,  $n_D^{25} 1.4454$ , whilst  $\alpha$ -monolaurin forms small, unctuous leaflets, m. p.  $62\text{--}63^\circ$  (Krafft, loc. cit., gives m. p.  $59^\circ$ , Grün and von Skopnik, A., 1909, i, 874,  $52^\circ$ , and Thieme, A., 1912, i, 333,  $58.9^\circ$ ).  $\alpha$ -Monolaurin is converted by phenylcarbimide into the diphenylurethane, small leaflets, which generally have m. p.  $87\text{--}89^\circ$ , but for which, on one occasion, the m. p.  $92\text{--}94^\circ$ , returning to the normal value after some weeks, was observed, and by stearyl chloride into  $\alpha$ -lauryl- $\beta\gamma$ -distearyl glycerol, m. p.  $49\text{--}50^\circ$ , apparently identical

with the product described by Grün and Theimer (A., 1907, i, 464). *Palmitylisopropylideneglycerol* crystallises in thin, irregular leaflets, m. p. 34—35°, whilst  $\alpha$ -monopalmitin resembles  $\alpha$ -monostearin in forming two modifications, m. p. 78—79° and 72—73°, respectively, which are prepared in the same manner as the stearyl compounds. It is transformed by lauryl chloride in the presence of chloroform and pyridine into  $\beta$ -*dilauryl- $\alpha$ -palmitylglycerol*, small, slender needles, m. p. 47—48°, after slight softening at 45°, the melting point of the solidified material being the same as that of the original substance.

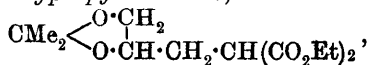
H. W.

**Acetone Glycerol [*iso*Propylideneglycerol] and its Applicability to the Preparation of Pure  $\alpha$ -Glycerides; A Compound of Phosphoric Acid and Glycol.** EMIL FISCHER and ERNST PFÄHLER (*Ber.*, 1920, 53, [B], 1606—1621).—The present communication is devoted to a general survey of the possibility of using *isopropylideneglycerol* in the syntheses of pure  $\alpha$ -monoglycerides (compare preceding abstract). Further confirmation of the constitution assigned to the substance by Irvine, Macdonald, and Soutar (*T.*, 1915, 107, 337) is found in that trimethylene glycol does not condense with acetone under conditions which readily yield products with ethylene and propylene glycols and with glycerol  $\alpha$ -chloro- and  $\alpha$ -iodo-hydrin. The introduction of the dihydroxypropyl complex into other substances appears to be most readily effected by means of *isopropylideneglycerol- $\alpha$ -iodo-hydrin*; the chlorine atom of the chlorohydrin is too firmly retained for this purpose.

*iso*Propylideneglycerol is prepared in 77% yield by the treatment of anhydrous glycerol with dry acetone containing 1% of hydrogen chloride in the presence of anhydrous sodium sulphate at the ordinary temperature; the bulk of the acid is removed by agitation with lead carbonate, and the filtrate is fractionated in the presence of a little silver oxide; the substance has b. p. 82.5°/11 mm.,  $D_4^{20}$  1.0678,  $D_4^{14}$  1.0721,  $n_D^{20}$  1.43509.

*iso*Propylideneglycerol- $\alpha$ -chlorohydrin, b. p. 157°/767 mm.,  $D_4^{15}$  1.109,  $D_4^{20}$  1.1079,  $n_D^{15}$  1.43750, is obtained from glycerol- $\alpha$ -chlorohydrin, b. p. 113°/10 mm. (which is conveniently prepared by the protracted boiling of *epichlorohydrin* with water); it is unaffected by aqueous acetone at 100°, and only slowly attacked by an excess of aqueous potassium hydroxide at 125° or by methyl-alcoholic ammonia at 100°. Protracted heating with sodium iodide and alcohol at 100° transforms it into glycerol- $\alpha$ -iodohydrin, m. p. 49—50°.

*iso*Propylideneglycerol- $\alpha$ -iodohydrin,  $\text{CMe}_2 \begin{smallmatrix} \text{O} \cdot \text{CH}_2 \\ \text{O} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{I} \end{smallmatrix}$  b. p. 79°/10 mm.,  $D_4^{15.5}$  1.652,  $D_4^{18.5}$  1.648,  $n_D^{15.5}$  1.50589,  $n_D^{18.5}$  1.50460, condenses with ethyl sodiomalonate in ethyl-alcoholic solution to *ethyl- $\beta$ -isopropylidenedioxypropylmalonate*,



h h 2

colourless oil, b. p. 155—156°/10 mm. (the *lead* salt, broad needles or leaflets, + H<sub>2</sub>O, and the *calcium* salt, needles, + 2.5H<sub>2</sub>O, of the corresponding acid, are described).

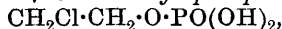
*iso*Propylideneglycerol acetate, mobile oil, b. p. 84°/9 mm., 87°/12 mm.,  $D_4^{15}$  1.0771,  $n_D^{15}$  1.42911, is obtained in 83% yield by the action of acetic anhydride and pyridine on *iso*propylideneglycerol, and is converted by *N*/4-sulphuric acid at 45° into  $\alpha$ -monoacetin, b. p. 103°/0.4 mm.; even at the lowest possible pressure, some slight decomposition occurs during distillation, and this increases rapidly in proportion as the pressure is raised. For synthetic purposes, it is therefore preferable to use the undistilled compound. (This observation makes it very probable that all the mono- and di-glycerides previously described, and purified by distillation under a pressure of 10 mm. and more, are not homogeneous.)  $\alpha$ -Monoacetin reacts with *p*-nitrobenzoyl chloride in the presence of chloroform and pyridine to yield *glyceryl*  $\beta\gamma$ -di-*p*-nitrobenzoate  $\alpha$ -acetate, microscopic, three-sided platelets, m. p. 129—130° (corr.); attempts to eliminate the acetyl group by methyl-alcoholic ammonia, and thus to obtain  $\alpha\beta$ -di-*p*-nitrobenzoylglycerol, did not lead to the desired results, since total alcoholysis occurred.

*iso*Propylideneglycerol is converted by phosphoryl chloride and quinoline at -20° into  $\beta\gamma$ -*iso*propylidenedioxypropyl phosphate,

$\text{CM}_{e_2} \begin{array}{l} \text{O} \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{PO}(\text{OH})_2 \end{array}$ , which is isolated in the form of

its *barium* salt, shining platelets (+ 3H<sub>2</sub>O); 3.64 parts of the anhydrous salt dissolve in 100 parts of water at 25°. The corresponding *silver*, *lead*, and *mercury* salts are described. The *barium* salt is transformed by sulphuric acid into  $\alpha$ -glyceryl phosphate, which is isolated as the readily soluble amorphous or sparingly soluble crystalline *barium* salt (the *silver* salt, colourless needles, is described). *Diisopropylideneglycerol* monophosphate is contained in the mother liquors obtained in the experiment just described, and is isolated as the readily soluble *barium* salt, C<sub>24</sub>H<sub>44</sub>O<sub>16</sub>P<sub>2</sub>Ba (the corresponding *lead*, *silver*, and *mercury* salts are described); acetone is removed by treatment with dilute sulphuric acid, thereby yielding *diglycerol* monophosphate, [OH·CH<sub>2</sub>·CH(OH)·CH<sub>2</sub>·O]<sub>2</sub>·PO·OH, which is obtained as the amorphous *barium* salt; the corresponding *silver*, *lead*, *mercury*, *copper*, and *zinc* salts are freely soluble in water.

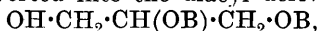
Ethylene glycol is transformed by phosphoryl chloride and pyridine at -20° into  $\beta$ -chloroethyl phosphate,



which is isolated as the *barium* salt, colourless needles (+ 3H<sub>2</sub>O); the corresponding *silver* salt, slender needles, and *lead* salt, colourless, amorphous precipitate, are described. H. W.

**Wandering of Acyl Groups in Glycerides.** EMIL FISCHER (*Ber.*, 1920, 53, [B], 1621—1633).—In previous syntheses of glycerides, it has generally been assumed that the acyl groups

retain their respective positions in the molecule when other substituents, such as halogen atoms, are removed. The observations of Fischer, Bergmann, and Lipschitz on the migration of acyl groups during the partial hydrolysis of acylated phenolcarboxylic acids (A., 1918, i, 172) have, however, cast some doubt on the general validity of this assumption, and it is now shown that similar instances of migration are encountered with glycerides. The problem is investigated in the following manner. On the one hand, an  $\alpha$ -monoacylglycerol,  $\text{OA} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$ , is converted by an acid chloride,  $\text{BCl}$ , in the presence of pyridine or quinoline into the mixed triglyceride,  $\text{OA} \cdot \text{CH}_2 \cdot \text{CH}(\text{OB}) \cdot \text{CH}_2 \cdot \text{OB}$ ; on the other hand, glycerol  $\alpha$ -iodohydrin is transformed by  $\text{BCl}$  into the diacyl iodohydrin,  $\text{CH}_2\text{I} \cdot \text{CH}(\text{OB}) \cdot \text{CH}_2 \cdot \text{OB}$ , which would be expected to be converted into the diacyl derivative,

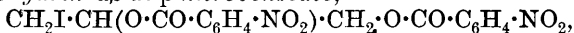


which, by treatment with  $\text{ACl}$ , should pass into the mixed triglyceride,  $\text{OA} \cdot \text{CH}_2 \cdot \text{CH}(\text{OB}) \cdot \text{CH}_2 \cdot \text{OB}$ , identical with that obtained by the first process. Actually, however, it is found that an isomeride of higher melting point and smaller solubility is produced, so that a displacement of an acyl group must have occurred during one of the changes. It appears probable that the migration of the acyl group from the  $\beta$ - to the  $\alpha$ -position occurs at the stage of the elimination of iodine, and although at present it is impossible to give an exact account of the mechanism of the change, it is suggested that an intermediate compound of the

type,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH} \begin{array}{c} \text{CH}_2 \cdot \text{O} \\ \text{---} \text{O} \end{array} \text{C} \begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{NO}_2 \\ \text{---} \text{OH} \end{array}$  (in the case of

the di-*p*-nitrobenzoyl derivative) is produced.  $\alpha\alpha'$ -Diglycerides are obtained with such readiness from  $\alpha\beta$ -diacyl- $\gamma$ -iodohydrins that this constitutes their readiest method of preparation. A somewhat similar series of actions has been effected by Grün and Schreyer (A., 1913, i, 159) with the corresponding chlorohydrins, but it is thus rendered highly probable that their " $\alpha\beta$ -diglycerides" are really  $\alpha\gamma$ -compounds.

*$\gamma$ -Iodohydrin  $\alpha\beta$ -di-*p*-nitrobenzoate,*



pointed needles, m. p.  $102-103^\circ$ , is obtained by the interaction of *p*-nitrobenzoyl chloride and  $\alpha$ -iodohydrin (alival) in the presence of chloroform and pyridine, and is converted by silver nitrite in boiling aqueous propyl-alcoholic solution or of silver acetate in the presence of warm glacial acetic acid into *glycerol  $\alpha\gamma$ -di-*p*-nitrobenzoate*,  $\text{OH} \cdot \text{CH}(\text{CH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$ , thin, colourless, four-sided, rhombic leaflets, m. p.  $136-137^\circ$  (corr.). The latter is converted by acetic anhydride in the presence of dry pyridine at the ordinary temperature into the corresponding  $\beta$ -acetyl derivative, long, slender needles, m. p.  $161^\circ$  (corr.).

*$\gamma$ -Iodohydrin  $\alpha\beta$ -distearate*, small needles, m. p.  $52-53^\circ$ , is similarly converted successively into  $\alpha\gamma$ -distearin, colourless, broad needles or platelets, m. p.  $78.5-79^\circ$  (corr.), and *glyceryl  $\beta$ -acetate  $\alpha\gamma$ -distearate*, silky needles, m. p.  $64^\circ$ . *Glyceryl  $\alpha$ -acetate  $\beta\gamma$ -*

*distearate* (from pure  $\alpha$ -monoacetin and stearyl chloride in the presence of chloroform and quinoline) crystallises in needles, m. p.  $59^{\circ}$ .

*Glyceryl  $\alpha$ -benzoate  $\beta\gamma$ -di-*p*-nitrobenzoate* crystallises in long, colourless needles, m. p.  $122$ — $123^{\circ}$  (corr.), whilst the isomeric *glyceryl  $\beta$ -benzoate  $\alpha\gamma$ -di-*p*-nitrobenzoate*, long, four-sided rods, has m. p.  $152$ — $152.5^{\circ}$  (corr.). Similarly, *glyceryl  $\alpha$ -*p*-nitrobenzoate  $\beta\gamma$ -distearate* forms slender, silky needles, m. p.  $74.5^{\circ}$ , and *glyceryl  $\beta$ -*p*-nitrobenzoate  $\alpha\gamma$ -distearate* crystallises in slender needles, m. p.  $61^{\circ}$ .  *$\gamma$ -Iodohydrin  $\alpha\beta$ -dibenzoate*, long, colourless needles, has m. p.  $56$ — $57^{\circ}$ . *Di-iodohydrin *p*-nitrobenzoate*, from *p*-nitrobenzoyl chloride and the di-iodohydrin (Jothion) in the presence of chloroform and pyridine, forms microscopic, four-sided prisms, m. p.  $82$ — $83^{\circ}$  (corr.).

H. W.

### Interaction of Ethylene and Selenium Monochloride.

HAROLD WILLIAM BAUSOR, CHARLES STANLEY GIBSON, and WILLIAM JACKSON POPE (T., 1920, 117, 1453—1456).

**The Influence of Electrolytic Dissociation on the Distillation in Steam of the Volatile Fatty Acids.** JOSEPH REILLY and WILFRED J. HICKINBOTTOM (*Sci. Proc. Roy. Dubl. Soc.*, 1920, 16, 120—130).—When dilute solutions of volatile fatty acids are distilled, they show deviations in their distillation constants. These results cannot be explained on the basis of the possible occurrence of molecular complexes in the solution or of hydration of the solute. The deviations are probably due to electrolytic dissociation, since the deviation increases with the dilution, and is most marked with acids possessing a comparatively large dissociation constant. The authors have deduced a mathematical expression to represent this dissociation during distillation, and thus to correct the distillation constant. Applying this correction, it is found that the distillation constant is practically independent of the dilution.

The addition of certain salts and acids increases the distillation constant of acetic acid, but the amount of increase is dependent on the nature of the salt added. The addition of a solution of copper sulphate containing 1 gram-mol. per litre to a dilute acetic acid solution causes a diminution in the distillation constant.

W. G.

**Preparation of Ethylidene Diacetate.** SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE ANCT. GILLIARD, P. MONNET ET CARTIER (D.R.-P. 322746; from *Chem. Zentr.*, 1920, iv, 437).—Acetylene is treated with acetic acid and mercury salts in the presence of catalysing agents, the use of mercuric acetate and sulphuric esters being particularly cited. Acetylene is very rapidly absorbed in the presence of methylene sulphate at  $40$ — $65^{\circ}$ , or of methyl sulphate at  $70$ — $80^{\circ}$ , and the harmful effect of free mineral acids is avoided. Ethylidene diacetate, purified by fractional distillation in a

vacuum after addition of sodium acetate, is obtained in almost theoretical yield. H. W.

### Anhydrides of the Higher Aliphatic Fatty Acids. III.

D. HOLDE and H. SMELKUS (*Ber.*, 1920, **53**, [B], 1889—1897).—The preparation and purification of the anhydrides of the higher fatty acids have been investigated, more particularly in connexion with their possible use as articles of food in place of the glyceride fats. The material employed was the mixture of fatty acids from linseed oil and commercial olein, which was purified by distillation under diminished pressure. Albitzky's method of dehydration by means of acetic anhydride at 150—160° was adopted, and it was found that the proportion of anhydride recommended (5·5 times that theoretically necessary) is undoubtedly in excess of that actually required; the crude anhydrides cannot be freed from acetic acid and excess of anhydride by treatment with steam, since they are thereby almost entirely converted into fatty acids, and the yields of anhydrides cannot be estimated by titration of the products with *N*/10- or *N*/20-alcoholic alkali, since the anhydride is slowly converted into a mixture of the ethyl ester and sodium salt of the fatty acid. Attempts to separate the anhydrides from the fatty acids by means of alcohol were not successful, since, although the fatty acids from linseed oil, for example, are completely soluble in 72% alcohol (by volume), whilst the anhydrides are almost insoluble, the solubility of the latter is considerably affected by the presence of the former, possibly also by the formation of ethyl esters. With stronger alcohol, the solubility of the anhydrides in the presence of the fatty acids is uniformly greatly increased. Distillation under diminished pressure is unsuitable for the separation of oleic anhydride and oleic acid, since the former is decomposed during the process; as this has also been shown to be the case with palmitic acid, it appears to be true generally for the higher fatty acids and their anhydrides. The only satisfactory method appears to consist in treating the mixtures with solid sodium carbonate or with aqueous solutions of the latter.

H. W.

### Anhydrides of the Higher Aliphatic Fatty Acids. IV.

D. HOLDE and IDA TACKE (*Ber.*, 1920, **53**, [B], 1898—1907. Compare preceding abstract).—Further experiments on the preparation and properties of the mixtures of fatty anhydrides, obtained by the action of acetic anhydride on the fatty acids of linseed and rape-seed oil and on oleic acid, are described, particularly with a view to the possibility of their substitution for fats as foods. The proportion of acetic anhydride can be reduced to 3·5 times that theoretically necessary without reducing the yield below 83·5% (possibly this proportion can be still further reduced and the dehydration performed under ordinary pressure). Excess of the reagents is removed by distillation under diminished pressure, and further purification of the anhydrides is effected by treatment

with powdered sodium carbonate or aqueous sodium carbonate solution (5%). The purity of the products is conveniently examined by determination of the molecular weight in benzene solution. The mixtures of anhydrides have generally a somewhat higher melting point than the fatty acids from which they are derived, and, at the ordinary temperature, are semi-solid and sometimes partly crystalline. The viscosity and volatility is about the same as those of the corresponding glycerides, which they also closely resemble in refractive index. They are decomposed by  $N/10$  or more dilute alcoholic alkali hydroxide solution into almost exactly equivalent amounts of alkali salt and ethyl ester of the fatty acids, but the so-called saponification number can be estimated accurately with  $N/2$ -alcoholic potassium hydroxide. Mixed anhydrides of the fatty acid and acetic acid are not present in the products.

H. W.

**The Alkali Lactates as Substitutes for Glycerol [Per- and Perka-glycerin].** CARL NEUBERG and ELSA REINFURTH (*Ber.*, 1920, 53, [B], 1783—1791).—Apart from its use in the production of explosives, glycerol is extensively applied technically to the production of plastic masses, as a lubricant, as a solvent for heating baths, for the preservation of anatomical preparations and surgical instruments, and for pharmaceutical purposes. Its many-sided applicability depends mainly on its viscosity, hygroscopicity, and neutral character. The shortage of natural sources of glycerol experienced by the Central Powers during the war has directed attention to possible substitutes, which have been found in aqueous solutions of the sodium and potassium salts of fermentation lactic acid (per- and perka-glycerin respectively). As generally prepared, both salts consist of colourless, viscous substances with a not unpleasant saline taste, which are stable at elevated temperatures, and pronouncedly hygroscopic. They only crystallise when in a very highly purified condition, and readily yield strongly supersaturated solutions, which are miscible in all proportions with water and alcohol. They are not poisonous, and do not irritate the membranes. They have this economic advantage over glycerol, that their preparation permits a much better utilisation of the initial material (sugar, etc.), since this can be so fermented as to yield 95% and more lactic acid, whilst, on the technical scale, it only gives one-fifth to one-fourth of its weight of glycerol; further, for many purposes, the glycerol substitutes can be used in more dilute solution than glycerol itself. An extended account is given of the application of the substitutes in the armies and navies of the Central Powers, and of their use for medical and cosmetic purposes, for details of which the original paper must be consulted; in general, however, it may be stated that they well fulfil all the non-explosive purposes to which glycerol is usually applied.

It has been observed during the industrial preparation of sodium and potassium lactates that these salts can be crystallised from highly concentrated aqueous solutions, but the solid preparations

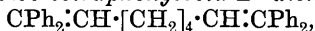
do not give uniform results on analysis, since the fermentation acid is a mixture of racemic and optically active lactic acids.

Tables and graphs are given showing the densities of aqueous solutions of "per- and perka-glycerin" at 15°, the freezing point of solutions of "perglycerin" at differing concentrations, the comparative freezing points of solutions of "perglycerin" and glycerol of similar molecular concentrations, the boiling points of solutions of "perglycerin," the comparative hygroscopicity of solutions of "perglycerin" and glycerol at 25°, and the viscosity of "perglycerin."

H. W.

**The Methodical Degradation of Saturated Dibasic Acids of High Molecular Weight.** MARCEL GODCHOT (*Compt. rend.*, 1920, 171, 797—799).—The method used by Bouvet and by Barbier and Locquin (*A.*, 1913, i, 700) for the conversion of saturated dibasic acids into corresponding acids containing two atoms less of carbon is found to be applicable to the higher acids in the series.

Thus, ethyl suberate yields with magnesium phenyl bromide *ααθθ-tetraphenyloctane-αθ-diol*, m. p. 112—113°. which, when dehydrated, gives *ααθθ-tetraphenylocta-Δ<sup>αθ</sup>-diene*,

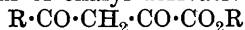


m. p. 92—93°, and this, on oxidation, gives adipic acid.

In a similar manner, ethyl azelate gives, in turn, *ααu-tetraphenylnonane-αi-diol*, m. p. 136°, *ααu-tetraphenylnona-Δ<sup>αi</sup>-diene*, b. p. 310°/20 mm.,  $D^{20}_D$  1.047, and pimelic acid, whilst ethyl sebacate gives *αακκ-tetraphenyldecano-ακ-diol*, m. p. 131—132°, *αακκ-tetraphenyldeca-Δ<sup>ακ</sup>-diene*, m. p. 107°, and suberic acid.

W. G.

**The Isomeric Forms of Mesityloxidoxalic Acid and its Esters.** W. DIECKMANN (*Ber.*, 1920, 53, [B], 1772—1782).—The  $\alpha$ - and  $\beta$ -forms of mesityloxidoxalic acid and its esters have generally been regarded as typical cases of keto-enolic desmotropy (compare Claisen, *A.*, 1896, i, 557; Dimroth, *A.*, 1907, i, 663; Michael and Hibbert, *A.*, 1907, i, 1010; 1908, i, 28; Michael and Murphy, *A.*, 1908, i, 949; K. H. Meyer, *A.*, 1911, i, 865). The  $\alpha$ -compounds are, beyond doubt, enolic forms, but, on the other hand, the conception of the  $\beta$ -compounds as ketones is no longer tenable. The behaviour of oxalyl derivatives of the type

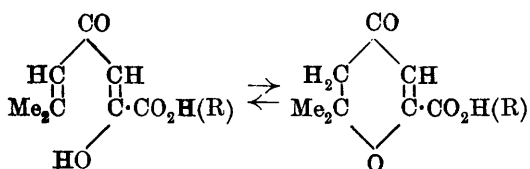


is generally in accordance with Claisen's rule that the tendency towards enolisation and the enol content of the equilibrium mixture increase with increasing acidity of the acyl groups; with mesityloxidoxalic esters, however, the equilibrium mixture contains only a small percentage of the enolic form, and, further, the  $\alpha$ -ester, when distilled, passes mainly into the neutral  $\beta$ -ester. It is likewise remarkable that, whereas the enolic forms of acetophenoneoxalic acid and propionylpyruvic acid can be crystallised unchanged from boiling water,  $\alpha$ -mesityloxidoxalic acid passes

*h h\**



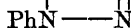
completely into the  $\beta$ -acid when treated in this manner. Similar anomalies are exhibited by  $\alpha$ -mesityloxidoxalic acid with respect to its rate of transformation in alcoholic solution; with substances of the type  $R \cdot CO \cdot CH_2 \cdot CO \cdot R'$ , equilibrium is generally established at  $25^\circ$  in the absence of catalysts within a day, and the rate of transformation is very greatly catalysed by alkaline agents, and to a very much smaller extent by acids; with  $\alpha$ -mesityloxidoxalic ester, the change proceeds so slowly at the atmospheric temperature that equilibrium is only attained after several months, the velocity of transformation is catalytically influenced to an unusually small degree by alkaline agents, but very markedly by acids, even at very small concentrations. It therefore appears that the  $\alpha$ - and  $\beta$ -forms cannot be regarded as keto-enolic desmotropes, and their



isomerism is attributed to the conversion of the  $\alpha$ -forms by ring closure into dihydro- $\gamma$ -pyrone derivatives, according to the annexed

scheme. This conception is in harmony with the observed equilibrium relationships and rates of transformation, and generally interprets the chemical behaviour of the  $\beta$ -forms better than does the ketonic formula. It thus explains Claisen's observation that the aniline salt of the  $\beta$ -acid, in contrast to that of the  $\alpha$ -acid, does not pass into the anil in hot alcoholic solution, and the fact that whereas  $\alpha$ -mesityloxidoxalic acid and its esters are readily converted by phenylhydrazine into phenylpyrazole derivatives, the  $\beta$ -acid and its esters yield normal phenylhydrazones, which do not pass into pyrazoles, even after protracted warming with glacial acetic acid. The physical properties of the  $\beta$ -forms are shown to be in harmony with the dihydropyrone formula. It is remarkable that Claisen, in his preliminary note on these compounds (*Ber.*, 1891, **24**, 115), considered that the  $\beta$ -varieties are dihydropyrone derivatives, but that this conception is abandoned in the subsequent fuller account (*loc. cit.*) in favour of the ketonic structure.

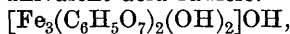
Methyl  $\alpha$ -mesityloxidoxalate is converted by phenylhydrazine in glacial acetic acid solution into methyl 1-phenyl-5- $\Delta^{\alpha}$ -isobutenylpyrazole-3-carboxylate,  $\text{Me}_2\text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{CO}_2\text{Me}$ , colourless



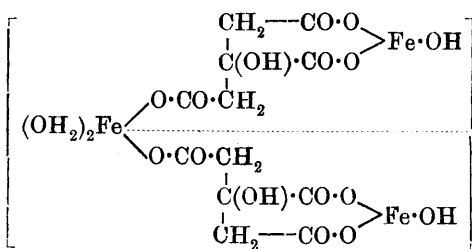
crystals, m. p.  $108^\circ$ , which is hydrolysed by alkali to the corresponding acid, colourless needles, m. p.  $167^\circ$  (which is also obtained from the  $\alpha$ -acid and phenylhydrazine in acetic or hydrochloric acid solution); the methyl ester of the  $\beta$ -compound gives the phenylhydrazone of methyl 2:2-dimethyl-2:3-dihydro- $\gamma$ -pyrone-6-carboxylate, intensely yellow crystals, m. p.  $163^\circ$ . H. W.

**Organic Salts of Iron. II. Ferric Citrates and Ammoniacal Ferric Citrates.** E. BELLONI (*Gazzetta*, 1920, **50**, ii, 159—212. Compare A., 1909, i, 283).—The author dis-

cusses the literature, dealing, first, with complex organic cations and anions containing iron, and, secondly, with the chemistry of the ferric and ammoniacal ferric citrates. All the hypotheses which have been advanced to explain the structure of ammoniacal citrates of iron are based on the existence of normal ferric citrate,  $C_6H_5O_7Fe$ , which has been assumed from the results of old, insecure analyses. The chemical behaviour of ferric citrate renders it probable that the iron is present as a complex cation, and the concordant results of analyses of different preparations of the citrate lead to the formula  $[Fe_3(C_6H_5O_7)_2(OH)_2]^{1/3}C_6H_5O_7 \cdot 8H_2O$ . The citrate represents, indeed, a dicitratoferric citrate, in which there appears a new term of the series of univalent cations,  $[Fe_3(OH)_2]^{X_3}$ , where X indicates a univalent acid radicle. The base,



of the citrate forms also a platinichloride, the existence of which confirms the fact that only one-seventh of the combined citric acid of the citrate is ionisable. The structure of the citratoferric ion must be analogous to that established in the case of ferric formate (*loc. cit.*), and confirmed by Weinland and Gussmann (A., 1909, i, 872; 1910, i, 296, 457, 537) and Herz (A., 1899, i, 416) for ferric and chromiferric acetates, and is shown in the annexed formula.



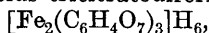
This complex ion differs from those of other organic iron salts in that the central iron atom is united to two citric radicles, which are held in the complex by both a principal and a secondary valency. Ferric citrate must hence be

regarded as an internal complex salt (compare Ley, A., 1905, i, 175), analogous to the cuprous compound of glycine (Bruni and Fornara, A., 1904, i, 855), to the cobaltous compounds of dimethylglyoxime (Tschugaev, A., 1906, i, 984), and to the compounds recently described by Werner and Matissen (A., 1918, i, 379). The chromic compound corresponding with this ferric compound has also been obtained.

As regards the red ammoniacal ferric citrate, obtained by addition of ammonia to a solution of the dicitratotriferric citrate, it is found that four molecules of any alkali are absorbed by the dicitratotriferric cation without disturbance of the equilibrium permitting of the existence of this complex; further addition of an energetic alkali destroys the complex, but excess of ammonia does not affect the new complex. The composition of the ammoniacal product, the fact that  $2H_2O$  is eliminated only at  $120^\circ$ , and its chemical properties, indicate that it is diquodiferryl-

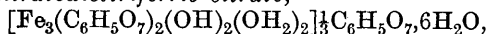
citratotetramminoferric citrate. With only 2 mols. of ammonia, ferric citrate forms diaquocitratoferrylcitratodiammino-oldiferric citrate. With both these ammoniacal ferric citrates, only one-seventh of the combined citric acid is ionisable, and the corresponding platinichlorides have been obtained. The tetrammino-citrate (1 mol.), like other ferric salts, is able to dissolve excess of ferric hydroxide (up to 6.66 mols.); the solutions thus obtained may be concentrated without undergoing change, and then yield scaly products, which increase in brittleness and opacity as the percentage of dissolved hydroxide increases.

The interaction in the hot of 2 mols. of ferric hydroxide and 3 mols. of citric acid yields tricitratodiferric acid,

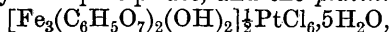


and treatment of this with 3 mols. of ammonia gives the triammonium ferricitrate,  $[\text{Fe}_2(\text{C}_6\text{H}_4\text{O}_7)_3](\text{NH}_4)_3\text{H}_3$ , which is the green ammoniacal ferric citrate used pharmaceutically. The monoammonium and diammonium salts were also prepared.

*Diaquodicitratodioltriferric citrate,*

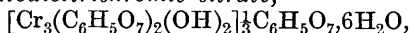


forms a reddish-yellow precipitate, and the *platinichloride*,



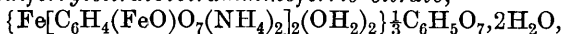
a reddish-brown, crystalline powder.

*Diaquodicitratodioltrichromic citrate,*



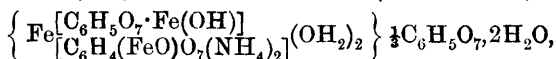
forms blue scales with a violet reflexion, and the *platinichloride*,  $[\text{Cr}_3(\text{C}_6\text{H}_5\text{O}_7)_2(\text{OH})_2(\text{OH}_2)_2]\frac{1}{3}\text{PtCl}_6, 5\text{H}_2\text{O}$ , a violet, crystalline powder.

*Diaquodiferrylcitratotetramminoferric citrate,*



forms garnet-red scales, and the corresponding *platinichloride*,  $\{\text{Fe}[\text{C}_6\text{H}_4(\text{FeO})\text{O}_7(\text{NH}_4)_2]_2(\text{OH}_2)_2\}\frac{1}{3}\text{PtCl}_6, 3\text{H}_2\text{O}$ , a reddish-brown, microcrystalline powder.

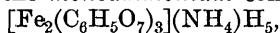
*Diaquocitratoferrylcitratodiamminodiferric citrate,*



forms large, reddish-brown scales, and the *platinichloride* a reddish-brown, microcrystalline powder.

*Tricitratodiferric acid*,  $[\text{Fe}_2(\text{C}_6\text{H}_4\text{O}_7)_3]\text{H}_6$ , forms yellowish-brown scales, and *trisodium* and *triammonium tricitratodiferrates*,  $[\text{Fe}_2(\text{C}_6\text{H}_4\text{O}_7)_3](\text{NH}_4)_3\text{H}_3$ , green scales.

*Diammonium tricitratodiferrate*,  $[\text{Fe}_2(\text{C}_6\text{H}_4\text{O}_7)_3](\text{NH}_4)_2\text{H}_4$ , is yellowish-green, and the *monoammonium* compound,



yellow; both are highly hygroscopic.

T. H. P.

**Aldol Condensation and Formation of Resin by the Action of Dilute Alkalis on Acetaldehyde.** HARALD HAMMARSTEN (*Annalen*, 1920, 421, 293—315).—In a previous paper (this vol., i, 710), the Cannizzaro reaction with acetaldehyde has been discussed, and the present communication deals mainly with the simultaneous formation of aldols and resin. The

materials which have been examined are acetaldehyde and acetaldol, acetone, and dimethylacetonylcarbinol,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{COME}$ , whilst the bases are the hydroxides of potassium, lead, and barium at  $0^\circ$ ,  $18^\circ$ , and  $50^\circ$ . The estimation of acetaldehyde in the presence of aldol cannot be accurately performed by simple distillation of the mixtures, since the latter is sensibly decomposed before the former is quantitatively volatilised. A convenient method consists in drawing a rapid stream of purified air through the mixture at  $25\text{--}30^\circ/25\text{--}30$  mm.; acetaldehyde is thereby volatilised, and is absorbed by a measured volume of  $N/5$ -iodine solution in the presence of  $N/1$ -potassium hydroxide, the excess of iodine being subsequently titrated with  $N/10$ -thiosulphate. A molecule of acetaldehyde reacts with four atoms of iodine apparently in accordance with the equation  $2\text{Me}\cdot\text{CHO} + 8\text{I} + 3\text{KOH} = 2\text{CHI}_3 + \text{H}\cdot\text{CO}_2\text{K} + \text{MeOH} + 2\text{KI} + 2\text{H}_2\text{O}$ . Acetaldehyde and aldol cannot be sufficiently sharply separated by extraction with ether, the respective partition coefficients between ether and water being 4.15 and 0.66. The aldols cannot be estimated titrimetrically or colorimetrically, and they are therefore determined by first removing the bulk of the resin by filtration of the solution, and then by exhaustive extraction with ether. The ethereal solution is dried, the solvent is removed at a low temperature, and the residue is weighed after being exposed to the action of phosphoric oxide at atmospheric pressure during twenty-four hours. The aldols are subsequently volatilised at  $120^\circ/10$  mm., and any residual resin is weighed. The possibility of applying the magenta-sulphurous acid colorimetric method to the estimation of aldols has been examined, and it is found that freshly distilled acetaldol gives a coloration about 0.65 times as intense as that of an equivalent amount of acetaldehyde; the higher aldols, however, do not give a coloration.

The results are given in a series of tables, for which the original paper must be consulted. It is shown that the chief reaction between dilute acetaldehyde and alkalis consists in the formation of aldols, and that this occurs with hydroxyl-ion concentrations, which are as low as  $2.5 \times 10^{-6}$  gram-ion per litre. The aldols are not utilised in subsequent reactions, such as formation of resin, even when the temperature is raised and the time of contact prolonged. Acetaldol is the primary condensation product, but it rapidly passes for the greater part into higher aldols, of which  $\text{OH}\cdot\text{CHMe}\cdot[\text{CH}_2\cdot\text{CH}(\text{OH})]_n\cdot\text{CH}_2\cdot\text{CHO}$  has been identified. Under the conditions adopted, less than 40% of aldols has never been obtained from 0.5*N*-acetaldehyde solution. It appears, therefore, that the more complex aldols cannot yield aldehyde resin, which is, however, produced from acetaldol.

The Cannizzaro reaction occurs far less rapidly than the aldol condensation, but appears to be relatively more noticeable with more concentrated than with dilute solutions of potassium hydroxide; with barium hydroxide, the influence of concentration is less marked. Lead hydroxide is peculiar, since it induces neither

Cannizzaro's reaction nor resin formation, although production of aldol is fairly rapid. Temperature appears to have about the same catalysing action on all the changes, and the final equilibrium is therefore independent of this factor.

The constitution of aldehyde resin has been further investigated; for this purpose, aqueous solutions of acetaldehyde (2*N*) are allowed to remain for five to six days with an equal volume of aqueous potassium hydroxide solution (10%) at the ordinary temperature. The solution is exactly neutralised with hydrochloric acid, whereby the ordinary red resin, m. p. about 120° (decomp.) after softening from 96°, is precipitated, which is identical with the  $\alpha$ - and  $\beta$ -aldehyde-resin described by Ekecrantz (A., 1912, i, 788). Further addition of a large volume of concentrated hydrochloric acid to the filtrate causes the separation of a very pale straw-yellow resin, which has m. p. 120—130° after softening at 105°, and commences to decompose above 200°. It appears to be a definite substance containing 66.13—66.73% C and 7.45—7.68% H, mol. wt. 396—412. The yellow resin appears to be first formed, since aldehyde solutions are initially coloured yellow by alkali and then clouded by the formation of a yellow precipitate, which darkens in colour as it increases in amount. It is uncertain whether the red resin is formed independently or through the yellow variety, but the former hypothesis is the more probable, since an alkaline solution of the yellow resin does not become turbid when preserved. The formation of aldehyde resin is not to be regarded as the final stage in the condensation of acetaldehyde; in solutions of the latter, the formation of acetate, ethyl alcohol, aldols, yellow and red resin, proceeds simultaneously.

Preliminary experiments with acetone indicate that, under the conditions adopted, an equilibrium is rapidly obtained between acetone and its condensation products in which not more than 14% of the former (at its boiling point) has undergone change. Complementary investigations with diacetone alcohol prove that this is a true equilibrium, and that this ketol is the main condensation product.

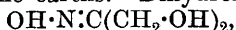
H. W.

**Process for the Purification of Acetone.** J. DUCLAUX and A. LANZENBERG (*Bull. Soc. chim.*, 1920, [iv], 27, 779—782).—The process is based on the fact that acetone forms with carbon disulphide a mixture with a minimum boiling point of 39°. To the acetone, 1.7 times its volume of carbon disulphide is added, and the mixture is distilled, all that passes over between 38° and 40° being collected in three fractions. From these three fractions the acetone is extracted by water, and the aqueous extracts are distilled, the fraction boiling at 56.1—56.3° being collected. Methyl alcohol also forms a mixture with carbon disulphide which has b. p. 37.5°, and if this alcohol is present as an impurity in the acetone, the above process must be modified. The minimum b. p. distillate is left over potassium carbonate for some time before extraction with water, and copper sulphate is added to the aqueous

extract before its fractionation. In this way, most of the methyl alcohol is removed. W. G.

**Researches on Residual Affinity and Co-ordination. II. Acetylacetones of Selenium and Tellurium.** GILBERT T. MORGAN and HARRY DUGALD KEITH DREW (T., 1920, 117, 1456—1465).

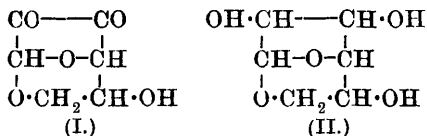
**Preparation of Dihydroxyacetoxime.** C. H. BOEHRINGER SOHN (D.R.-P. 322845; from *Chem. Zentr.*, 1920, iv, 437).— $\beta$ -Nitropropylene glycol or one of its salts is treated with reducing agents in the presence of basic substances, such as the hydroxides of the alkalis or alkaline earths. Dihydroxyacetoxime,



is almost quantitatively convertible into glycerol.

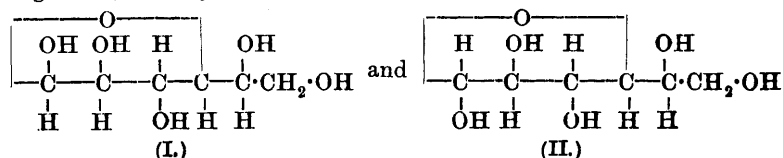
H. W.

**Constitution of Lævoglucosan.** AMÉ PICTET and MARC CRAMER (*Helv. Chim. Acta*, 1920, 3, 640—644).—Lævoglucosan, obtained by Tanret (A., 1894, i, 564) and by Vongerichten and Müller (A., 1906, i, 198) by hydrolysing certain glucosides, by Pictet and Sarasin (A., 1918, i, 59) by distilling cellulose or starch under reduced pressure, and by Karrer (this vol., i, 370) by distilling  $\beta$ -glucose in a vacuum, reacts with excess of acetyl chloride, giving  $\beta$ -acetochloroglucose (compare Skraup and Kremann, A., 1901, i, 506). When heated on a water-bath with neutral or faintly alkaline permanganate solution, lævoglucosan yields a syrupy compound, which does not reduce Fehling's solution, is neutral to litmus, reacts with phenylhydrazine, giving the *diphenylhydrazone*,  $\text{C}_{18}\text{H}_{18}\text{O}_3\text{N}_4$ , m. p. 154—155°, yields a basic, crystalline compound when treated with *o*-phenylenediamine,



and is converted into a crystalline acetate by acetic anhydride. Formula I is attributed to this oxidation product and formula II to lævoglucosan itself. T. H. P.

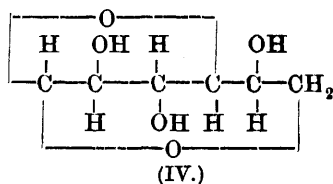
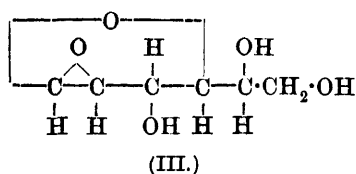
**Configuration of  $\alpha$ - and  $\beta$ -Glucoses.** AMÉ PICTET (*Helv. Chim. Acta*, 1920, 3, 649—652).—That, of the two formulæ for *d*-glucose, namely,



(I) represents the  $\alpha$ - and (II) the  $\beta$ -modification, is indicated by the following observations: (1) Tanret (A., 1895, i, 490) found that, at 110°,  $\alpha$ -glucose is slowly converted into the  $\beta$ -form; since

similar atoms or groups of atoms tend to repel one another, this transformation is more probably from (I) to (II) than from (II) to (I). (2) Böeseken (A., 1913, i, 1147) found that, in order that an alcohol may increase the electrical conductivity of boric acid solutions, it must possess at least two hydroxyl groups attached to two neighbouring carbon atoms and situate in the same plane and on the same side of the carbon atom chain; as  $\alpha$ -glucose exhibits this property, it should have formula (I).

The accuracy of these indications is proved as follows by the author, the only assumption made being that the hydroxyls of glucose are able to react one with another, with loss of the elements of a molecule of water, only when such hydroxyls occur on the same side of the plane formed by the hydrofuran nucleus. With  $\alpha$ -glucose there corresponds an anhydride, glucosan (compare Pictet and Castan, this vol., i, 594), which, having lost the hydroxyl groups attached to the first and second carbon atoms, possesses the grouping of an ethylene oxide, and can thus only have the structure (III). Lævoglucosan (preceding abstract), the anhydride of  $\beta$ -glucose, does not contain the primary alcoholic group of glucose, and corresponds with the configuration (IV). It is hence evident that  $\alpha$ - and  $\beta$ -glucoses correspond, respectively, with formulæ I



and II. The two anhydrides, differing so greatly in structure, are best termed, for the present, glucosan and lævoglucosan, and not, as suggested by Vongerichten and Müller (*loc. cit.*) and others,  $\alpha$ - and  $\beta$ -glucosans. T. H. P.

**The Influence of Different Substances on the Decomposition of Monoses by an Alkali and on the Inversion of Cane Sugar by Hydrochloric Acid.** H. I. WATERMAN and J. GROOT (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 149—161).—A study of the influence of *o*-phthalic acid,  $\alpha$ - and  $\beta$ -naphthoic acids, cinnamic acid, *o*-coumaric acid, 1:2- and 2:3-hydroxynaphthoic acids, Schäffer salt, *G*-salt, and sodium phenol-*p*-sulphonate, respectively, on the decomposition of dextrose by alkali, and of the influence of 1:2- and 2:3-hydroxynaphthoic acids, cinnamic acid, *o*-coumaric acid, *o*-phthalic acid,  $\alpha$ - and  $\beta$ -naphthol, and  $\alpha$ -naphthoic acid, respectively, on the inversion of sucrose by hydrochloric acid. W. G.

**Polysaccharides. I. Methylation of Starch.** P. KARRER (*Helv. Chim. Acta*, 1920, **3**, 620—625).—The author has succeeded in methylating starch by treating it with methyl iodide and silver oxide in water, or with methyl sulphate and baryta water, etc. In

this way, three preparations have been obtained containing 1, about 1.5, and 2 methoxyl groups, respectively, per  $C_6H_{10}O_5$ . The first is readily soluble only in cold water, the second dissolves also to some extent in alcohol, and the third is readily soluble in water, alcohol, or chloroform. Fehling's solution is not reduced by any of these compounds or by the mother liquors from which they are obtained. With iodine they give, respectively, reddish-violet, brownish-yellow, and almost imperceptibly yellow colorations. Preliminary molecular-weight determinations of the third preparation indicate the value 1000—2000.

The author considers that the crystalloid starch can be broken down into molecules only when soluble derivatives are prepared, the process of dissolution effecting the depolymerisation. His view of the highly polymeric polysaccharides is to some extent similar to that of Hess and Wittelsbach (this vol., i, 532), but it should be unnecessary to employ a new name like "cellulose" to designate the true cellulose or starch molecule, such molecule differing from cellulose or starch only as a molecule does from a crystal (this vol., i, 370).

T. H. P.

**Lignin and Reactions of Lignin. II.** PETER KLASON (*Ber.*, 1920, **53**, [B], 1862—1863. Compare this vol., i, 148, 474).—The author has previously described the isolation of the naphthylamine salt,  $CH_2R \cdot CH \begin{matrix} \swarrow SO_2-O \\ \searrow CH \cdot NH \cdot C_{10}H_7 \end{matrix}$ , from the lignin of the pine, and has now obtained similar compounds from fir, birch, beech, oak, linden, alder, and aspen, the composition of which, as indicated by estimation of nitrogen and sulphur, is practically the same in every case. Although the lignin of these different varieties is certainly not identical, it therefore appears that it invariably belongs to the same type. The lignin of herbaceous plants likewise yields yellow, cyclic arylammonium salts, but their composition differs considerably from that of those obtained from trees.

H. W.

**Constitution of Pine Lignin.** PETER KLASON (*Ber.*, 1920, **53**, [B], 1864—1873).—The portion of lignin which contains an acraldehyde group, and in the form of its sulphonic acid yields cyclic arylammonium salts, is termed acraldehyde lignin or  $\alpha$ -lignin; it is identical with the constituent that yields the calcium lignosulphonate precipitable by calcium chloride. The second lignin present in wood, the calcium sulphonate of which is not precipitable by calcium chloride, and does not give a cyclic salt, but contains a carboxyl group, is named carboxylignin or  $\beta$ -lignin.

The formula  $C_{22}H_{22}O_7$  is deduced for  $\alpha$ -lignin in the following manner. The author's analyses of calcium lignosulphonate give results in agreement with the formula  $C_{40}H_{44}O_{18}S_2Ca$  [and thus harmonising with Hönig and Spitzer's analyses (*A.*, 1918, i, 375) of the barium and calcium salts]; the lignin residue contained in the salt must thus have the composition  $C_{20}H_{20}O_6$  or  $C_{20}H_{22}O_6$ , and since it is known that an acetyl group is removed from lignin





ammonium radicle, the author has electrolysed a solution of tetraethylammonium chloride in anhydrous liquid ammonia in a specially designed cell, which is so arranged as to exclude atmospheric air, the details of which are promised in a subsequent communication (compare McCoy and West, A., 1912, i, 539; Palmaer, A., 1903, i, 12). Dark blue streaks are immediately formed at the platinum cathode, and a dark bluish-black solution is ultimately obtained, which retains its colour during several hours at  $-78^{\circ}$ . It exhibits strong absorption in the violet and red. When the solution is evaporated at about  $-100^{\circ}$ , slow decomposition takes place, and the residue consists solely of unchanged chloride; at  $-33^{\circ}$ , a mixture of tetraethylammonium chloride and triethylamine remains, showing that decomposition occurs according to the scheme  $2\text{NEt}_4 = 2\text{NEt}_3 + \text{C}_4\text{H}_{10}$ , and therefore in the same manner as with the simple ammonium radicle. The solution instantly reacts with iodine, giving tetraethylammonium iodide. If a current of dry oxygen is passed over the cathode, the blue streaks disappear immediately, and, after removal of the solvent, a pale yellow residue remains, which appears to contain very little of the tetraethylammonium peroxide (as would be expected from analogy with similar experiments with potassium salts), and to consist of unchanged chloride mixed with about 70% of tetraethylammonium hydroxide. The coloration is also discharged by acetylene, but a compound analogous to potassium acetylide does not appear to be formed. Tetramethyl- and tetra-*n*-propylammonium iodides behave similarly when subjected to electrolysis, but with phenyltriethylammonium iodide, diethylaniline immediately separates at the cathode. Attempts to obtain the free radicles by the action of potassium, sodium, or calcium on solutions of tetraalkylammonium salts in liquid ammonia have not been successful up to the present. The replacement of ammonia by pyridine or chloroform has not given satisfactory results.

H. W.

### Glycine and its Additive Compounds with Neutral Salts.

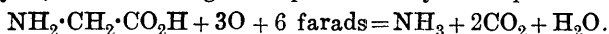
HAROLD KING and ALBERT DONALD PALMER (*Biochem. J.*, 1920, **14**, 574—583).—In the main, the results of Pfeiffer and Modelski (A., 1912, i, 949; 1913, i, 709) regarding the definite nature of the compounds of glycine with calcium, barium, and strontium chlorides of the type  $\text{MCl}_2 \cdot (\text{C}_2\text{H}_5\text{O}_2\text{N})_2 \cdot \text{H}_2\text{O}$ , and with lithium chloride and bromide of the types  $\text{LiCl}(\text{or Br}) \cdot \text{C}_2\text{H}_5\text{O}_2\text{N} \cdot \text{H}_2\text{O}$  and  $\text{LiCl}(\text{or Br}) \cdot (\text{C}_2\text{H}_5\text{O}_2\text{N})_2 \cdot \text{H}_2\text{O}$ , are confirmed. Additive compounds with potassium haloids were not obtained, but with sodium bromide and iodide, compounds,  $\text{NaBr} \cdot (\text{C}_2\text{H}_5\text{O}_2\text{N})_2 \cdot \text{H}_2\text{O}$ , needles, and  $\text{NaI} \cdot (\text{C}_2\text{H}_5\text{O}_2\text{N})_2 \cdot \text{H}_2\text{O}$ , needles, were obtained. A compound with calcium iodide,  $\text{CaI}_2 \cdot (\text{C}_2\text{H}_5\text{O}_2\text{N})_2 \cdot 3\text{H}_2\text{O}$ , was isolated in the form of large, clear tablets.

Glycine usually crystallises in the monoclinic system, but when recrystallised from water it often separates in long needles or columns devoid of water of crystallisation. This is an unstable form, and gradually passes into the stable monoclinic form. The

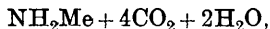
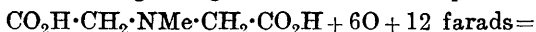
purest stable glycine which the authors have prepared decomposes in the neighbourhood of  $256^{\circ}$  (uncorr.). There is progressive darkening from about  $240^{\circ}$  onwards.

The observations of Falk and Sugiura (A., 1918, i, 292) are not confirmed.  
J. C. D.

**Behaviour of Glycine and its Allies on Electrochemical Oxidation.** FR. FICHTER and MAX SCHMID (*Helv. Chim. Acta*, 1920, 3, 704—714).—Electrolysis of a solution of glycine in *N*-sulphuric acid yields (1) a mixture of ammonia and various methylamines, the mixed chlorides of these being evidently what was regarded by Lilienfeld (A., 1904, i, 295) and by Kühling (A., 1905, i, 417) as ethylenediamine hydrochloride; (2) formic acid; (3) formaldehyde; and (4) carbon dioxide and monoxide. The initial reaction is expressed by the equation  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H} + \text{O} + 2 \text{ farads} = \text{NH}_3 + \text{CH}_2\text{O} + \text{CO}_2$ . The heat generated at the anode then causes interaction of the formaldehyde and ammonia, a mixture of mono-, di-, and tri-methylamine being produced (compare Plöchl, A., 1888, 1051); a similar mixture of bases may, indeed, be obtained by electrolytic oxidation of a mixture of formaldehyde and ammonium sulphate solution. As the electrolysis proceeds, the yields of ammonia and carbon dioxide diminish, the former the more rapidly, owing to progressive oxidation of the formaldehyde; the final stage is represented by the equation



Electrolysis of aqueous sodium acetylaminooacetate solution gives carbon dioxide in greater yields than, and ammonia in about the same yields as, with glycine; acetic acid, formaldehyde, and formic acid are detectable among the products. Similarly, iminodiacetic acid undergoes rapid and complete oxidation according to the equation  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} + 6\text{O} + 12 \text{ farads} = 4\text{CO}_2 + \text{NH}_3 + 2\text{H}_2\text{O}$ . Methyliminodiacetic acid gives ammonia, methylamine, and carbon dioxide in good agreement with the equation



and with  $\alpha$ -aminoisobutyric acid the electrolysis corresponds with the equation  $\text{NH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H} + \text{O} + 2 \text{ farads} = \text{NH}_3 + \text{CMe}_2 + \text{CO}_2$ .

$\alpha$ -*p*-Toluenesulphonylaminoisobutyric acid,  $\text{C}_{11}\text{H}_{15}\text{O}_4\text{NS}$ , prepared by the interaction of  $\alpha$ -aminoisobutyric acid and *p*-toluenesulphonyl chloride in alkaline solution, crystallises in long, white needles, m. p.  $147^{\circ}$ .  $\alpha$ -Benzenesulphonylaminoisobutyric acid,  $\text{C}_{10}\text{H}_{13}\text{O}_4\text{NS}$ , similarly prepared, forms white needles, m. p.  $144^{\circ}$ .  $\alpha$ -Benzenesulphonylmethylaminoisobutyric acid,  $\text{C}_{11}\text{H}_{15}\text{O}_4\text{NS}$ , prepared by treating the previous compound with methyl iodide and sodium hydroxide solution, crystallises in needles, m. p.  $171^{\circ}$ . When aqueous solutions of the sodium salts of the first and last of these three acids are electrolysed, both undergo profound oxidation, with liberation of sulphuric acid, which causes separation of the slightly soluble organic acid at the anode, and thus disturbs

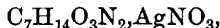
the electrolysis. In the former case ammonia, and in the latter methylamine, is formed from the beginning in amounts corresponding with those of the carbon dioxide and sulphuric acid produced, so that here, too, the attack commences at the nitrogen atom.

With  $\beta$ -alanine, ammonia, carbon dioxide, acetic acid, and formaldehyde are produced, the ratio between carbon dioxide and ammonia indicating complete destruction of the carbon chain. Benzoyl- $\beta$ -alanine, as sodium salt, is only slowly attacked on electrolysis, the darkening which occurs indicating removal and hydroxylation of the benzoyl group; ammonia appears immediately.

Electrochemical oxidation of the amino-acids may be compared with the oxidative desamination which these compounds undergo in the living organism, but is far more vigorous and profound. The results obtained show with certainty that Kolbe's synthesis cannot be effected with aliphatic amino-acids (compare A., 1918, i, 369).

T. H. P.

**The Methylation of Dipeptides.** A. KOSSEL and S. EDLBACHER (*Zeitsch. physiol. Chem.*, 1919, **107**, 45—51).—Glycylglycine hydrochloride was treated with methyl sulphate in the presence of sodium hydroxide. After two hours, the mixture was acidified with hydrochloric acid, evaporated to dryness under diminished pressure, and the residue then extracted with methyl alcohol in order to separate the sodium methyl sulphate; a colourless syrup was eventually obtained. The methylated product was precipitated as the picrate, from which it was afterwards liberated and crystallised from alcohol, m. p. 141°. The aurichloride,  $C_7H_{14}O_3N_2 \cdot HAuCl_4$ , melted at 155°. The argentonitrate,



has m. p. 180°. The free base, on hydrolysis with sulphuric acid, yielded, amongst other products, glycine and betaine. The methylation of *dl*-alanylglycine was carried out in the same way as that of glycylglycine. The aurichloride,  $C_8H_{18}O_4N_2 \cdot HAuCl_4$ , obtained has m. p. 105°. On hydrolysis with sulphuric acid, glycine and *dl*-trimethyl- $\alpha$ -propiobetaine, m. p. 240°, were obtained. In both instances, three methyl groups were therefore introduced into the dipeptide.

S. S. Z.

***d*-Glutamic Acid.** L. HUGOUNENQ and G. FLORENCE (*Bull. Soc. chim.*, 1920, [iv], **27**, 750—754).—*d*-Glutamic acid may best be isolated from its hydrochloride by evaporating the hydrochloride on a water-bath with an alcoholic solution of aniline, and extracting the residue with hot water. The glutamic acid separates on cooling. Calcium glutamate gives with calcium chloride a double salt,  $C_{10}H_{16}O_8N_2Ca \cdot CaCl_2 \cdot 2H_2O$ ,  $[\alpha]_D - 2 \cdot 25^\circ$ . If a solution of the hydrochloride is saturated with freshly precipitated cupric hydroxide, a copper derivative,  $(C_5H_9O_4N)_5 \cdot 4CuO \cdot 7\frac{1}{2}H_2O$ , is obtained as small, blue crystals. Barium, zinc, and cadmium salts of glutamic acid, and mercury, cobalt, and nickel derivatives, have been prepared.

W. G.

**The Direct Synthesis of Carbamide by Urease.** H. P. BARENDRECHT (*Rec. trav. chim.*, 1920, **39**, 603—605).—A reply to Mattaar (this vol., i, 537). W. G.

**The Constitution of Carbamides. XIII. The Constitution of Cyanic Acid, and the Formation of Urea from the Interaction of Ammonia and Cyanic Acid at Low Temperatures.** EMIL ALPHONSE WERNER and WILLIAM ROBERT FEARON (*T.*, 1920, **117**, 1356—1362).

**The Interaction of Carbon Disulphide and Ammonium Carbonate.** FRANÇOIS A. GILFILLAN (*J. Amer. Chem. Soc.*, 1920, **42**, 2072—2079).—Carbon disulphide and ammonium carbonate interact at 160°, giving a mixture of ammonium thiocyanate and thiocarbamide. The equilibrium depends on the concentration of the reagents used, the temperature and duration of heating, and the concentration of the hydrogen sulphide produced in the reaction. The yield of thiocarbamide is much below the theoretical value, and the method is not recommended. The reversion to ammonium thiocyanate is favoured by the presence of hydrogen sulphide.

The estimation of ammonium thiocyanate cannot be carried out accurately by the indirect titration method in a mixture containing more than 15% of thiocarbamide. Direct titration with silver nitrate, however, gives satisfactory results with mixtures containing as much as 40% of thiocarbamide. The interference is apparently due to the solubility of silver thiocyanate in thiocarbamide solutions.

In solutions containing not more than 5 mg. of thiocarbamide per 100 c.c., this substance may be estimated by titration with iodine. W. G.

**Some Thiocyanates of Silver with Ammonium and Sodium.** RADU CERNATESCU (*Bull. Acad. Sci. Roumaine*, 1920, **6**, 53—56).—The author has prepared two double thiocyanates of silver and sodium, NaCNS,AgCNS and 3NaCNS,AgCNS, and of silver and ammonium, NH<sub>4</sub>CNS,AgCNS and 5NH<sub>4</sub>CNS,AgCNS. From the last salt, the silver is not precipitated by the addition of barium chloride. W. G.

**New Synthesis of Hydrogen Cyanide by Catalysis.** ALPH. MAILHE and F. DE GODON (*Bull. Soc. chim.*, 1920, [iv], **27**, 737—739).—When carbon monoxide and ammonia are passed together over thorium oxide at 410—450°, an excellent yield of ammonium cyanide is obtained. The thorium oxide may be replaced by aluminium oxide or zirconium oxides, but a higher temperature is then necessary. W. G.

**A Sparingly Soluble Double Salt of Calcium Ferrocyanide and Calcium Ferrite.** G. GRUBE [with L. BAUMEISTER and E. LÄMLE] (*Zeitsch. anorg. Chem.*, 1920, **112**, 245—261).—When Prussian-blue is decomposed with excess of calcium hydroxide into soluble calcium ferrocyanide and ferric

hydroxide, a side reaction occurs, the calcium ferrocyanide combining with the ferric hydroxide and excess of calcium hydroxide to form a sparingly soluble, white precipitate. As this is only stable in presence of excess of calcium hydroxide, and is decomposed by water, with formation of ferric hydroxide, it could not be isolated for analysis. By estimating the quantity of calcium ferrocyanide precipitated from solution by known quantities of ferric and calcium hydroxides, it was established that the constituents are present in the double salt in the proportion  $\text{Ca}_2\text{Fe}(\text{CN})_6:2\text{Ca}(\text{OH})_2:4\text{Fe}(\text{OH})_3$ , and that the compound probably consists of a double salt of calcium ferrocyanide and calcium ferrite,  $2\text{CaFe}_2\text{O}_4, \text{Ca}_2\text{Fe}(\text{CN})_6$ . The composition was confirmed by determinations of the change of hydroxyl-ion concentration in a calcium hydroxide solution caused by adding ferric hydroxide and calcium ferrocyanide. There is no evidence of the formation of calcium ferrite when ferric hydroxide is added to a saturated solution of calcium hydroxide. When calcium ferrocyanide is added to the mixture, the hydroxyl-ion concentration falls, and there is a break in the curve at the point corresponding with the composition  $\text{Ca}_2\text{Fe}(\text{CN})_6:2\text{Ca}(\text{OH})_2:4\text{Fe}(\text{OH})_3$ . E. H. R.

**Cyanoacetylene,  $\text{C}_3\text{HN}$ .** CHARLES MOUREU and JACQUES CH. BONGRAND (*Ann. Chim.*, 1920, [ix], **14**, 47—58).—A more detailed account of work already published (A., 1911, i, 22). W. G.

**Dicyanodimethyl Sulphide.** WILHELM STEINKOPF (*Ber.*, 1920, **53**, [B], 1671).—The substance, described by Steinkopf, Herold, and Stöhr in their recent communication (this vol., i, 523), has been prepared previously and in a similar manner by von Zweigbergk (A., 1913, i, 24). H. W.

**Carbon Subnitride,  $\text{C}_4\text{N}_2$ .** CHARLES MOUREU and JACQUES CH. BONGRAND (*Ann. Chim.*, 1920, [ix], **14**, 5—47).—A more detailed account of work already published (compare A., 1910, i, 159; 1914, i, 671; this vol., i, 425). W. G.

**The Freezing Point of Wet Benzene, and the Influence of Drying Agents.** NEVIL VINCENT SIDGWICK (T., 1920, **117**, 1340—1343).

**The System Benzene-Ethyl Alcohol-Water between +25° and -5°.** NEVIL VINCENT SIDGWICK and WILLIAM JAMES SPURRELL (T., 1920, **117**, 1397—1404).

**The Catalytic Action of Iodine in Sulphonation. I.** JÑANENDRA NATH RÂY and MANIK LAL DEY (T., 1920, **117**, 1405—1407).

**Use of Catalysts in the Sulphonation of Aromatic Compounds.** JOSEPH A. AMBLER and WILLIAM J. COTTON (*J. Ind. Eng. Chem.*, 1920, **12**, 968—969).—The sulphonation of benzene in 70% sulphuric acid at 242—259° is accelerated by the addition of various catalysts in a concentration of 0.1% of the active element. The presence of compounds of the following elements slightly

increased the proportion of benzene sulphonated: copper, mercury, vanadium, chromium, potassium, and lithium, whilst a mixture of sodium sulphate and vanadium pentoxide had a pronounced effect. The catalytic action of sodium and potassium sulphates is not entirely due to their raising the boiling point of the sulphuric acid. The results indicated that members of the first group of the periodic system, represented by sodium and lithium, accelerated the formation of disulphonic acid, whilst the mixture of vanadium pentoxide and sodium sulphate was still more effective, but the other catalysts tried apparently inhibited the formation of that acid. C. A. M.

**Preparation of certain Esters of Benzenesulphonic Acid.** ZOLTÁN FÖLDI (*Ber.*, 1920, **53**, [B], 1836—1839).—The substances are conveniently prepared by the gradual addition of aqueous sodium hydroxide solution (20—30%) to a cold, well-stirred mixture of benzenesulphonyl chloride and the requisite alcohol until the mixture is permanently alkaline; the product is subsequently mechanically shaken for some hours, and the ester is ultimately distilled under diminished pressure. It is somewhat surprising to note that the method can be readily applied even with the halogenhydrins.

*Allyl benzenesulphonate* forms a colourless oil, D 1.166, which decomposes ultimately, with explosive violence, when distilled under diminished pressure.  $\beta$ -*Chloroethyl benzenesulphonate*,  $\text{SO}_2\text{Ph}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ , has b. p.  $184^\circ/9$  mm.,  $D_4^{15}$  1.353, whilst the corresponding *bromo-ester* has b. p.  $192^\circ/20$  mm.,  $185\text{—}187^\circ/16$  mm.,  $D_4^{15}$  1.575.  $\beta\beta'$ -*Dichloroisopropyl benzenesulphonate*,  $\text{SO}_2\text{Ph}\cdot\text{O}\cdot\text{CH}(\text{CH}_2\text{Cl})_2$ , long, colourless needles, m. p.  $50^\circ$ , b. p.  $200\text{—}205^\circ/20$  mm., is very resistant towards hydrolysing agents.

In the case of  $\beta$ -chloroethyl benzenesulphonate, the benzenesulphonyl group is removed about four times as readily by alcoholic sodium hydroxide solution as is the chlorine atom, whilst in  $\beta\beta'$ -dichloroisopropyl benzenesulphonate the chlorine atom is less firmly retained than the benzenesulphonyl radicle. H. W.

***s*-Bromobenzenedisulphonic Acid.** S. C. J. OLIVIER and K. J. B. DE KLEERMAEKER, jun. (*Rec. trav. chim.*, 1920, **39**, 640—645. Compare Herzig, A., 1882, 46).—When bromobenzene is boiled with concentrated sulphuric acid under a reflux condenser for eight hours, 5-bromobenzene-1:3-disulphonic acid is obtained, which gives a *disulphonyl chloride*, m. p.  $99\text{—}100^\circ$ , a *diamide*, m. p.  $255\text{—}256^\circ$ , and *barium*, *potassium*, and *lead* salts. The disulphonyl chloride, when heated with phosphorus pentachloride, yields *s*-trichlorobenzene. W. G.

**Possible Influence of Electronegative Groups on the Mobility of the Methylene Hydrogen Atoms in Arylsulphonated Methylene Derivatives.** J. TRÖGER and E. NOLTE (*J. pr. Chem.*, 1920, [ii], **101**, 136—157. Compare Tröger and Vasteling, A., 1905, i, 870; Tröger and Beck, A., 1913, i, 630; Tröger and Wunderlich, A., 1915, i, 792).—It is found that the

methylene hydrogen atoms are not mobile in sulphones of the general formula  $X \cdot C_6H_4 \cdot SO_2 \cdot CH_2Ph$  or  $X \cdot C_6H_4 \cdot SO_2 \cdot CH_2 \cdot C_6H_4X$  (in which X is a nitro- or hydroxyl group or a halogen atom). Apparently the substituents are too far removed to exert an effect on the methylene group; when, however, they are brought nearer, as in compounds of the type  $R \cdot SO_2 \cdot CH_2 \cdot NO_2$  and  $R \cdot SO_2 \cdot CH_2 \cdot CN$ , the resulting substances are soluble in alkali and readily undergo condensation.

*Benzenesulphonyl-m-nitrophenylmethane*,  $SO_2Ph \cdot CH_2 \cdot C_6H_4 \cdot NO_2$ , is prepared by the action of *m*-nitrobenzyl chloride on sodium benzenesulphinate in boiling alcoholic solution; it forms colourless, shining needles, m. p.  $163^\circ$ , whilst the corresponding *o*- and *p*-derivatives consist of colourless needles, m. p.  $113^\circ$ , and crystalline crusts, m. p.  $207^\circ$ , respectively. The isomerides are insoluble in aqueous sodium hydroxide solution (15%); attempts to methylate the *ortho*-compound by methyl iodide and sodium ethoxide at  $100^\circ$ , or to bring it into action with benzenediazonium chloride, were unsuccessful. Reduction with tin and fuming hydrochloric acid transforms the nitro-compounds into the corresponding amino-derivatives, of which the *o*-isomeride forms discoloured needles, m. p.  $174^\circ$  (*hydrochloride*, irregular leaflets), the *m*-base crystallises in coarse, pale brown needles, m. p.  $139^\circ$  (*hydrochloride*, colourless needles grouped to aggregates), and the *p*-isomeride (previously described by Hinsberg and Himmelschein as aminotolylphenylsulphone) has m. p.  $176^\circ$ ; attempts to methylate the latter by methyl iodide and sodium ethoxide at  $100^\circ$  were completely unsuccessful, and did not even affect the free amino-group. Benzenesulphonyl-*m*-aminophenylmethane is converted in the usual manner into *benzenesulphonyl-m-hydroxyphenylmethane*, small, discoloured needles, m. p.  $125^\circ$ , which is converted by an excess of methyl iodide and sodium ethoxide at  $100^\circ$  into *benzenesulphonyl-m-methoxyphenylmethane*, yellowish-white leaflets, m. p.  $109^\circ$ .

Attempts are described to prepare *benzenesulphonylnitromethane*,  $SO_2Ph \cdot CH_2 \cdot NO_2$ , by the action of chloronitromethane on sodium benzenesulphinate in the presence of a little alcohol, but grave difficulties are caused by the acidic nature of the latter, and the yields are very poor; the products are partly soluble and partly insoluble in sodium hydroxide solution, and, from the former, two substances, colourless crystals, m. p.  $151^\circ$  and m. p.  $69-72^\circ$ , respectively, have been isolated, which give analytical results in agreement with those required by benzenesulphonylnitromethane. The substance of lower m. p. reacts with benzenediazonium chloride to yield a reddish-yellow, crystalline product, which is either a hydrazone or an azo-compound, and the formation of which demonstrates the mobility of the hydrogen atoms of the parent substance. Somewhat better results are obtained when the reaction is applied to sodium *p*-bromobenzenesulphinate; in this instance, *p*-bromobenzenesulphonylnitromethane is isolated in colourless, shining needles, m. p.  $161^\circ$ , although the yields are



poor. The substance dissolves in aqueous sodium hydroxide solution, and with benzenediazonium chloride gives a *product*, golden-yellow needles, m. p.  $164^{\circ}$ , which is probably to be regarded as the hydrazone,  $C_6H_4Br \cdot SO_2 \cdot C(N \cdot NPh) \cdot NO_2$ , since it dissolves in cold sodium hydroxide solution to form a *sodium salt*, thin, yellow needles.

The following substances were prepared from their components with the object of investigating the conjoint influence of a halogen atom in the phenylsulphonyl group and a nitro-group in the phenyl radicle attached to the methylene group: *p*-chlorobenzenesulphonyl-*p*-nitrophenylmethane,  $C_6H_4Cl \cdot SO_2 \cdot CH_2 \cdot C_6H_4 \cdot NO_2$ , colourless needles, m. p.  $162^{\circ}$ ; *p*-chlorobenzenesulphonyl-*m*-nitrophenylmethane, shining leaflets, m. p.  $179^{\circ}$ ; *p*-chlorobenzenesulphonyl-*o*-nitrophenylmethane, yellowish-white, irregular crystals, m. p.  $137^{\circ}$ ; *p*-bromobenzenesulphonyl-*o*-nitrophenylmethane, plates, m. p.  $137^{\circ}$ ; *p*-bromobenzenesulphonyl-*m*-nitrophenylmethane, colourless, crystalline powder, m. p.  $182^{\circ}$ ; *p*-bromobenzenesulphonyl-*p*-nitrophenylmethane, microcrystalline powder, m. p.  $195^{\circ}$ ; *p*-iodobenzenesulphonyl-*o*-nitrophenylmethane, small, colourless leaflets, m. p.  $129^{\circ}$ ; *p*-iodobenzenesulphonyl-*m*-nitrophenylmethane, colourless, shining needles, m. p.  $218^{\circ}$ ; *p*-iodobenzenesulphonyl-*p*-nitrophenylmethane, brownish-yellow needles, m. p.  $223.5^{\circ}$ . Certain of these have been reduced by tin and fuming hydrochloric acid in glacial acetic acid solution, yielding thereby: *p*-bromobenzenesulphonyl-*p*-aminophenylmethane, pale yellow needles, m. p.  $187^{\circ}$  (*hydrochloride*, silvery crystals); *p*-bromobenzenesulphonyl-*m*-aminophenylmethane, leaflets, m. p.  $146^{\circ}$  (*hydrochloride*, silvery crystals); *p*-bromobenzenesulphonyl-*o*-aminophenylmethane, leaflets (*hydrochloride*, coarse, prismatic, yellow needles). *p*-Bromobenzenesulphonyl-*p*-hydroxyphenylmethane, yellowish-white, uncharacteristic crystals, m. p.  $194.5^{\circ}$ , is obtained by the diazotisation of the corresponding amine at  $60-70^{\circ}$  under pressure, and subsequent heating of the diazonium solution; its solubility in sodium hydroxide solution appears to be due solely to the presence of the phenolic hydroxyl group.

*p*-Toluenesulphonyl-*m*-nitrophenylmethane forms colourless octahedra, m. p.  $162^{\circ}$ , whilst the corresponding *o*- and *p*-nitrophenyl derivatives crystallise in yellowish-white needles, m. p.  $132^{\circ}$ , and small, colourless, shining needles, m. p.  $182^{\circ}$ , respectively.

The effect of the presence of a nitro-group in the arylsulphonyl radicle has been investigated at the instance of the following compounds: *p*-nitrophenylbenzylsulphone, m. p.  $169^{\circ}$ , obtained by the oxidation of *p*-nitrophenyl benzyl sulphide by permanganate, which, contrary to the observations of Fromm and Wittmann (A., 1908, i, 631), is not methylated by treatment with methyl iodide and sodium ethoxide at  $100^{\circ}$ ; *m*-nitrobenzenesulphonylphenylmethane, yellowish-white, silky needles, m. p.  $160^{\circ}$  (*m*-aminobenzenesulphonylphenylmethane, colourless, pointed needles, m. p.  $119.5^{\circ}$ ); *m*-nitrobenzenesulphonyl-*p*-nitrophenylmethane, brown platelets, m. p.  $192^{\circ}$ ; *m*-nitrobenzenesulphonyl-*o*-nitrophenyl-

*methane*, brown crystals, m. p.  $184^{\circ}$ ; *m-nitrobenzenesulphonyl-m-nitrophenylmethane*, yellowish-white needles, m. p.  $171^{\circ}$ .

*m-Nitrobenzenesulphonylacetonitrile*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{CH}_2 \cdot \text{CN}$ , is obtained with unexpected difficulty and in poor yield by the action of chloroacetonitrile on sodium *m*-nitrobenzenesulphinate at  $130^{\circ}$ ; the mobility of its methylene hydrogen atoms is proved by its solubility in aqueous alkali, its power to condense with aldehydes to form substances, such as *m-nitrobenzenesulphonylanisylidene-acetonitrile*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{C}[\text{CH} \cdot \text{C}_6\text{H}_4(\text{OMe})] \cdot \text{CN}$ , pale yellow, silky needles, m. p.  $160^{\circ}$ , and its ability to react with benzene-diazonium chloride to give *m-nitrobenzenesulphonylbenzeneaz-acetonitrile* (or the *phenylhydrazone* of *m-nitrobenzenesulphonylformyl cyanide*), reddish-yellow needles, m. p.  $175^{\circ}$ , which form salts with bases.

H. W.

### Modification and Extension of the Friedel and Crafts' Reaction. I. JNANENDRA NATH RÂY (T., 1920, 117, 1335—1339).

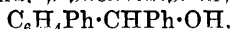
**Organic Molecular Compounds. II.** JAMES F. NORRIS and DOROTHY M. TIBBETTS (*J. Amer. Chem. Soc.*, 1920, 42, 2085—2092).—It has been shown that tetraphenyldichloroethane forms well-characterised molecular compounds with chloroform and carbon tetrachloride (A., 1911, i, 31), and later that other organic compounds of certain types, such as tetra-*p*-bromophenylethylene, possesses to a high degree the power to form molecular compounds (A., 1916, i, 380). The authors propound the following hypothesis in explanation. The molecular compound is formed as a result of the coming into play of latent affinities residing on an atom in each of the constituents of the compound. All atoms possess these latent affinities, but whether or not they are of such a nature as to permit the union of a molecule with a second molecule is determined by the extent to which the chemical energy of the atom in question has been expended in the formation of the molecule containing it. In the case of unsaturated compounds containing a double linking, the molecular compounds are most often formed by direct addition, but sometimes their formation is due only to the latent chemical affinity of the double bond.

In addition to the molecular compounds previously described, it is now shown that tetra-*p*-bromophenylethylene forms well-crystallised molecular compounds with toluene, *p*-xylene, chlorobenzene, ethyl ether, ethyl and propyl acetates, and ethyl propionate, but not with chloroform, ethyl or amyl alcohol, bromo- or iodo-benzene, *m*-xylene, light petroleum, methyl acetate, or ethyl formate. This method may therefore be employed in separating ethyl alcohol from acetone and *p*-xylene from *m*-xylene. If the bromine is replaced by chlorine, the ability to form molecular compounds is much reduced. Tetra-*p*-chlorophenylethylene only formed additive products with benzene, carbon tetrachloride, and methyl ethyl ketone.

Triphenyl-*p*-chlorophenylethylene only formed a molecular com-

pound with carbon tetrachloride, and tetraphenylethylene did not give any molecular compounds. It should be noted that whereas triphenylchloromethane forms molecular compounds, the corresponding bromo-derivative does not.

Triphenylchloromethane and triphenylcarbinol both give molecular compounds, but the corresponding diphenyl compounds do not. On the other hand, *p*-phenyldiphenylcarbinol,



and *p*-phenyldiphenylchloromethane,  $\text{C}_6\text{H}_4\text{Ph}\cdot\text{CHPhCl}$ , both yield molecular compounds with carbon tetrachloride. *p*-Bromodiphenylcarbinol and di-*p*-chlorophenylcarbinol did not give molecular compounds.

W. G.

### Relationship of Retene to the Resin Acids. Hydrogenated Retenes. ARTTURI J. VIRTANEN (*Ber.*, 1920, 53, [B], 1880—1889).

—A considerable number of hydrogenated retenes have been prepared with the ultimate object of elucidating their relationship to the resin acids, the literature of which is exhaustively reviewed. With the exception of tetrahydroretene, the substances are stable towards permanganate, which is rather surprising, in view of the fact that some of them, at any rate, are unsaturated. Attempts to prepare picrates of the hydrocarbons were unsuccessful in every case.

*Dihydroretene*,  $\text{C}_{18}\text{H}_{20}$ , colourless, shining leaflets, m. p. 64—65°, b. p. 188—190°/10 mm., is obtained by the action of sodium on a boiling solution of retene in amyl alcohol; it is oxidised by chromic acid in glacial acetic acid solution to retenequinone. Tetrahydroretene, prepared in a similar manner, but with a larger proportion of sodium, is a yellow oil with a peculiar, very unpleasant odour, b. p. 180—183°/10 mm.,  $D_4^{20}$  1.0057,  $n_D^{20}$  1.56061. The more highly hydrogenated retenes are obtained from the parent hydrocarbon, fuming hydriodic acid ( $D$  1.96), and red phosphorus under varied conditions of temperature and relative proportions of reagents; *hexahydroretene*, colourless oil, b. p. 175—177°/10 mm.,  $D_4^{20}$  0.9802,  $n_D^{20}$  1.54705; *octahydroretene*, colourless oil, b. p. 163—165°/10 mm.,  $D_4^{20}$  0.9578,  $n_D^{20}$  1.53023; *decahydroretene*, colourless oil, b. p. 155—158°/10 mm.,  $D_4^{20}$  0.9342,  $n_D^{20}$  1.51501; and *dodecahydroretene*, colourless oil, b. p. 148—150°/10 mm.,  $D_4^{20}$  0.8985,  $n_D^{20}$  1.48510, are described. Tetra-, hexa-, octa-, and deca-hydroretenes appear to be nitrated by warm concentrated nitric acid, towards which the dodeca-compound is stable.

H. W.

### Geometrical Isomerism of Polymethylenes. A. SKITA (*Ber.*, 1920, 53, [B], 1792—1806).—In general, chemical methods for the preparation of the various stereoisomeric derivatives of cyclohexane are at present unknown, and it is not possible to obtain any selected stereoisomeride at will from a definite initial material. Since the recent investigations of von Auwers (A., 1919, i, 578) have afforded trustworthy physical methods of placing

isomerides in the *cis*- or *trans*-series, it appeared desirable to apply a number of different methods to the reduction of the same unsaturated substance with the object of classifying the processes in accordance with their tendency to produce *cis*- or *trans*-isomerides. For this purpose, 2:4:5-trimethylaniline has been selected. It is reduced by hydrogen in the presence of colloidal platinum in strongly acid solution to 2:4:5-trimethylcyclohexylamine; on the other hand, it is converted by nitrous acid into 2:4:5-trimethylphenol, which is similarly reduced to 2:4:5-trimethylcyclohexanol (the corresponding hydrocarbon and ketone are also described), which differs from the similar series obtained by Auwers (this vol., i, 721) from 2:4:5-trimethylphenol by Sabatier's process in that the individual members have relatively greater density and index of refraction and smaller molecular refraction, and are therefore characterised as *cis*-compounds, whilst those described by von Auwers belong to the *trans*-series. The oxime of the author's *cis*-1:2:4-trimethylcyclohexane-5-one is reduced in acid solution to the amine, obtained from  $\psi$ -cumidine (which is thus also a *cis*-compound), but with sodium and alcohol it gives an isomeric base, which is regarded as *trans*-5-amino-*cis*-1:2:4-trimethylcyclohexane. Similarly, 1:2:4-trimethylcyclohexane-5-one yields *trans*-5-hydroxy-*cis*-1:2:4-trimethylcyclohexane in acid solution, and *trans*-5-hydroxy-*cis*-1:2:4-trimethylcyclohexane in alkaline solution; the former is identical with the product obtained by the catalytic hydrogenation of  $\psi$ -cumenol in acetic acid solution in the presence of colloidal platinum, but the latter differs from the product prepared by Sabatier's process, which is to be regarded as 5-hydroxy-*trans*-1:2:4-trimethylcyclohexane.

It therefore appears justifiable to conclude that reduction of double bonds in acid solution favours the production of *cis*-forms, whilst *trans*-varieties are preferentially obtained in alkaline or neutral media; this generalisation, however, has only been tested up to the present for hydrocarbons, alcohols, and amines.

[With WILHELM HENNENBRUCH.]—The following substances are described: 1:2:4-trimethylcyclohexane, b. p. 33°/11 mm., 144·8—145·8° (corr.)/760 mm.,  $D_4^{20}$  0·790,  $n_D^{20}$  1·434; *cis*-5-hydroxy-*cis*-1:2:4-trimethylcyclohexane, b. p. 84°/17 mm., 191—193° (corr.)/760 mm.,  $D_4^{20}$  0·912,  $n_D^{20}$  1·463 (*phenylurethane*, m. p. 83·5°); *cis*-1:2:4-trimethylcyclohexane-5-one, b. p. 193° (corr.),  $D_4^{20}$  0·905,  $n_D^{20}$  1·450 (*semicarbazone*, needles, m. p. 204°; *oxime*, m. p. 105°); *trans*-5-hydroxy-*cis*-1:2:4-trimethylcyclohexane, b. p. 112°/35 mm., 196° (corr.)/760 mm.,  $D_4^{20}$  0·906,  $n_D^{20}$  1·461 (*phenylurethane*, m. p. 95°; *hydrogen phthalate*, m. p. 81—83·5°). *cis*-5-Amino-*cis*-1:2:4-trimethylcyclohexane, from 1:2:4-trimethyl-5-cyclohexylamine, or *cis*-1:2:4-trimethylcyclohexane-5-one oxime in acid solution by sodium amalgam or hydrogen and colloidal platinum, b. p. 74°/17 mm., 188—190° (corr.)/760 mm.,  $D_4^{20}$  0·864,  $n_D^{20}$  1·462 (*picrate*, m. p. 212° after softening at 208°; *hydrochloride*, m. p. 227—228°; *d*- $\alpha$ -bromocamphor- $\pi$ -sulphonate, colourless needles, m. p. 171·5°; *acetyl* derivative, needles, m. p. 100°;

*benzoyl* derivative, m. p. 107·5—108°; *phenylcarbamide*, oil; *phenylthiocarbamide*, needles, m. p. 164°; *trans-5-amino-cis-1:2:4-trimethylcyclohexane*, m. p. 21°, b. p. 187—188°/760 mm.,  $D_4^{20}$  0·857,  $n_D^{20}$  1·458 (*hydrochloride*, decomp. 260°; *d-α-bromocamphor-π-sulphonate*, decomp. 205—210°; *benzoyl* derivative, needles, m. p. 174·5°; *phenylcarbamide*, needles, m. p. 169°; *phenylthiocarbamide*, m. p. 155°); *trans-5-hydroxy-cis-1:2:4-trimethylcyclohexane*, formed, together with small amounts of 1:2:5-trimethylcyclohexene, b. p. 149° (corr.), by the action of sodium nitrite on the corresponding amine hydrochloride, b. p. 196° (corr.)/760 mm.,  $D_4^{20}$  0·906,  $n_D^{20}$  1·461 (*phenylurethane*, m. p. 95°; *hydrogen phthalate*, m. p. 81—83°); *cis-5-amino-cis-trans-1:2:4-trimethylcyclohexane*, obtained as by-product of the catalytic hydrogenation of 2:4:5-trimethylaniline, b. p. 181—182° (*picrate*, m. p. 153°; *phenylthiocarbamide*, m. p. 110°). H. W.

**Some Physical Constants of Pure Aniline.** C. L. KNOWLES (*J. Ind. Eng. Chem.*, 1920, **12**, 881—883).—Aniline solidifies at  $-6·24°$ , and has b. p. 184·32—184·39°/760 mm.,  $D_{15}^{15}$  1·0268,  $n_D^{20}$  1·5850. The solidifying point appears to be the best criterion of the purity of aniline, and this constant may be used as a basis for the estimation of actual aniline in a sample. The impurities most frequently found in commercial aniline are nitrobenzene, toluidine, and water; assuming the average molecular weight of these impurities to be 82·67, the percentage ( $X$ ) of aniline is found by the formula  $X = 108·79 + 1·41t$ , where  $t$  is the observed solidifying point. W. P. S.

### Crystalline Form of 2:4-Dibromo-3-nitroacetanilide.

MARIA DE ANGELIS (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 47—53. Compare this vol., i, 608).—This compound is not isomorphous with the corresponding dichloro-compound, but forms crystals,  $D$  2·131, belonging to the pinacoidal class of the triclinic system,  $a : b : c = 1·2526 : 1 : 1·0013$ ,  $\alpha = 96°54'$ ,  $\beta = 104°39'$ ,  $\gamma = 108°35'$ . Mixtures of the dichloro- and the dibromo-compounds form monoclinic crystals completely isomorphous with those of the  $\beta$ -modification of the dichloro-derivative. T. H. P.

**Some Condensation Products of Aromatic Aldehydes and Amines.** F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 74—83).—With a view of studying the polymorphism or isomerism of Schiff's bases, the author has prepared the following compounds and studied their crystallographic and optical properties.

*o*-Hydroxy-*m*-methylbenzylideneaniline (compare Anselmino, A., 1906, i, 13; 1907, i, 913) is obtained in red, monoclinic, prismatic crystals,  $a : b : c = 0·2362 : 1 : 0·6579$ ,  $\beta = 74°9\frac{1}{2}'$ ,  $D_4^{17}$  1·263, m. p. 74°, and in yellow (metastable), rhombic-bipyramidal crystals,  $a : b : c = 0·3732 : 1 : 0·4228$ ,  $D_4^{17}$  1·243, m. p. 70°. By the action of methyl sulphate, it yields *o*-methoxy-*m*-methylbenzylideneaniline, m. p.

70°, pale yellow, monoclinic-prismatic crystals,  $a:b:c = 1.2792:1.10509$ ,  $\beta = 76^\circ 59\frac{1}{2}'$ ,  $D_4^{16}$  1.166. When acted on with magnesium methyl iodide, it gives *o*-hydroxy-*m*-methyl- $\alpha$ -anilinoethylbenzene,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CHMe}\cdot\text{NHPh}$ , m. p. 90°, monoclinic-prismatic crystals,  $a:b:c = 0.2682:1.07254$ ,  $\beta = 85^\circ 47'$ ,  $D_4^{17}$  1.107. *o*-Methoxy-*m*-methyl- $\alpha$ -anilinoethylbenzene, m. p. 78°, gives rhombic-bipyramidal crystals,  $a:b = 0.3301:1$ ,  $D_4^{16}$  1.098. *o*-Hydroxybenzylideneaniline, m. p. 50.5° (compare Duparc, *Annalen*, 1891, 266, 140), occurs in two forms,  $\alpha$ -form, rhombic-bipyramidal crystals,  $a:b:c = 0.4729:1.02188$ ,  $D_4^{16}$  1.087;  $\beta$ -form, monoclinic-prismatic crystals,  $a:b = 2.4641:1$ ,  $\beta = 26^\circ 2\frac{1}{2}'$ ,  $D_4^{17}$  1.184. On methylation, it gives  $\alpha$ -anilinoethylanisole, m. p. 46°, rhombic-bipyramidal crystals,  $a:b:c = 0.884:1.0465$ ,  $D_4^{18}$  1.141. *p*-Methoxybenzylideneaniline, m. p. 63°, occurs in monoclinic-prismatic crystals,  $a:b:c = 1.5745:1.08063$ ,  $\beta = 65^\circ 21'$ ,  $D_4^{17}$  1.165. W. G.

**Action of Aluminium Chloride on Solutions of Aromatic Nitrohydrocarbons in Aromatic Hydrocarbons.** A. KLIEGL and HANS HUBER (*Ber.*, 1920, 53, [B], 1646—1655).—It has been shown by Freund that *p*-aminodiphenyl, in addition to much resinous matter, is formed when aluminium chloride acts on a boiling solution of nitrobenzene in benzene. In the hope of obtaining further insight into the action, the authors have repeated Freund's experiments, with the substitution of toluene for benzene, and have thus obtained *p*-aminophenyl-*p*-tolyl, which differs, however, from the similarly named substance prepared independently by Bamberger (*A.*, 1895, i, 289) and Kühling (*A.*, 1895, i, 182); the latter compound is shown to be *p*-aminophenyl-*o*-tolyl. The mechanism of the reaction is not yet fully elucidated, but progress has been made by the isolation of *N*-phenyl-*p*-toluidine as a by-product; it therefore appears that  $\beta$ -phenylhydroxylamine is intermediately formed, which in part condenses immediately, in part after transformation to *p*-aminophenol (or at the instant of transformation), with the aromatic hydrocarbon, with elimination of water:  $\text{NHPh}\cdot\text{OH} + \text{C}_6\text{H}_5\text{Me} = \text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me} + \text{H}_2\text{O}$  and  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH} + \text{C}_6\text{H}_5\text{Me} = \text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_5 + \text{H}_2\text{O}$ . It is definitely proved that *N*-phenyl-*p*-toluidine and *p*-aminophenyl-*p*-tolyl are formed when a solution of  $\beta$ -phenylhydroxylamine in toluene is treated with aluminium chloride, but, on the other hand, pre-formed *p*-aminophenol is not condensed with aromatic hydrocarbons by aluminium chloride, with formation of *p*-aminodiphenyls. It therefore appears that, at the instant at which the hydrogen atom and the hydroxyl group in  $\beta$ -phenylhydroxylamine leave their positions in the primary stage of the transformation, the aromatic hydrocarbon attaches itself to the free valency of the residual molecule.

Anhydrous aluminium chloride is gradually added to a boiling mixture of nitrobenzene and toluene; the product is poured into water, and unused materials are removed in a current of steam. The aqueous solution is filtered from resin and cooled, whereby

*p*-aminophenyl-*p*-tolyl hydrochloride is deposited in silvery leaflets, which rapidly become discoloured; the free base forms colourless crystals, m. p. 99°, b. p. 190°/18 mm. (*acetyl* derivative, colourless crystals, m. p. 221°). The residues from the condensation, when treated with superheated steam, give a small amount of *N*-phenyl-*p*-toluidine, slender, colourless needles, m. p. 88–89°. *p*-Hydroxyphenyl-*p*-tolyl, silvery leaflets, m. p. 154–155° (*benzoyl* derivative, colourless, shining leaflets, m. p. 188°), is prepared by the diazotisation of the base described above, and treatment of the diazonium salt with water. The same phenol is obtained from diazotised *p*-toluidine and phenol by Hirsch's method (D.R.-P. 58001), whilst *o*-toluidine, under similar treatment, gives *p*-hydroxyphenyl-*o*-tolyl, slender, colourless needles, m. p. 84–85° (*benzoyl* derivative, colourless needles, m. p. 89°), which is identical with the product obtained from Bamberger's base. The *para*-position of the methyl group in the authors' base is thus definitely established, whilst the position of the amino-group (and hence of the hydroxy-group in the phenol) follows from the analogous production of *p*-aminodiphenyl and from the identity of the base with that obtained by reduction of the product obtained by nitrating 4-methyldiphenyl. The latter substance, colourless leaflets, m. p. 49–50°, is obtained by the action of nitrosoacet-*p*-toluidide on benzene.

4-Amino-3:4'-dimethyldiphenyl, m. p. 42–43°, is obtained from *o*-nitrotoluene and toluene; the *acetyl* derivative crystallises in colourless needles, m. p. 206°. H. W.

**Manufacture of 4-Nitro- $\beta$ -naphthol.** GILBERT THOMAS MORGAN and BRITISH DYESTUFFS CORPORATION, LTD. (Brit. Pat. 152437).—2:4-Dinitro- $\alpha$ -naphthylamine, which may be obtained by the action of alcoholic ammonia at 220° on 2:4-dinitro- $\alpha$ -naphthol, or by the nitration and subsequent hydrolysis of aceto- $\alpha$ -naphthalide, is treated with nitrosyl sulphate or sodium nitrite in concentrated sulphuric acid, and the solution added to water to precipitate 4-nitronaphthalene-1-diazo-2-oxide. On warming this diazo-oxide with ethyl alcohol, either alone or in presence of a metallic catalyst, such as zinc, copper, aluminium, or a zinc-copper couple, or of a reducing agent, such as hypophosphorous acid, it is converted into 4-nitro- $\beta$ -naphthol, which is purified by extraction with hot water, from which it crystallises in yellow needles, m. p. 120°. 4-Nitro- $\beta$ -naphthol couples with the diazo-derivatives of substances such as sulphanilic acid, *p*-nitroaniline, safranin, and dianisidine, giving azo-compounds, which are of value as dyes for cotton, wool, and silk. G. F. M.

**Manufacture of Anthranol.** ARTHUR GEORGE PERKIN (Brit. Pat. 151707).—Anthranol is obtained by heating anthraquinone (60 parts) with dextrose (60 parts), and a 30% solution of sodium hydroxide (650 parts), in an autoclave provided with stirring gear, at 230° for five to ten hours. The product is then precipitated from the reaction mixture by the addition of hydrochloric acid

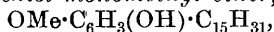
or by leading in carbon dioxide. Instead of dextrose in this reaction, sucrose, molasses, maltose, lactose, and the like may be used with similar results.  
G. F. M.

**The Determination of the Configuration of Cyclic *cis*- and *trans*-Diols and the Rearrangements of Atoms and Groups of Atoms during Chemical Reactions.** J. BÖRSEKEN and CHR. VAN LOON (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 69—73).—The effect of stereoisomeric diols on the conductivity of boric acid, or their behaviour on condensation with an active carbimide, or on condensation with acetone, may be used as a means of distinguishing between the *cis*- and *trans*-forms. As a rule, the *cis*-form augments the conductivity of boric acid, yields only one urethane, and readily yields a condensation product with acetone. In this way, the authors show that *cis*-hydrindenediol has m. p. 108°, *cis*-cyclopentanediol has m. p. 29—30°, and that, contrary to the statement of Brunel, the *cis*-form of cyclohexanediol is apparently the one having m. p. 99°. The method of preparation of diols by the oxidation of cyclopentene or cyclohexene appears to yield in each case the *cis*-form.  
W. G.

**Derivatives of Phenylldihydroresorcin.** ALEXANDER JOHN BOYD, PERCY HERBERT CLIFFORD, and MAURICE ERNEST PROBERT (*T.*, 1920, **117**, 1383—1390).

**The Main Constituent of Japanese Lac. VII. Urushiol Monomethyl Ether and the Mechanism of the Oxidation of Urushiol.** RIKŌ MAJIMA and GITARO TAKAYAMA (*Ber.*, 1920, **53**, [B], 1907—1916. Compare A., 1916, i, 38, and previous abstracts).—One of the two hydroxyl groups of urushiol is more readily methylated than the other, and the compound obtained by partial methylation is shown by a comparison of the properties of its tetrahydro-derivative with those of 2-hydroxy-*m*-tolyl methyl ether (Majima and Okazaki, A., 1916, i, 808) to be 2-hydroxy-3-methoxyurushiol (annexed formula). The tolyl derivative is shown to be oxidisable to a series of derivatives of diphenoquinone, and as precisely similar phenomena are observed during the oxidation of hydrourushiol, it appears valid to conclude that analogously constituted products are also formed in this case.

Urushiol is heated with sodium ethoxide and methyl sulphate in ethyl-alcoholic solution, and the monomethyl ether is separated from unchanged material and the dimethyl ether by fractional distillation under greatly reduced pressure; the slightly impure product is catalytically reduced by hydrogen in the presence of platinum to hydrourushiol monomethyl ether,

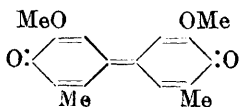


colourless needles, m. p. 44·5—45°, which is also obtainable by the partial hydrolysis of hydrourushiol dimethyl ether with



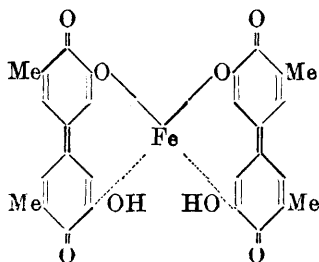
hydriodic acid (D 1.7). *Hydrourushiol monomethyl ether acetate* crystallises in colourless leaflets, m. p. 45.5—46.5°.

2-Hydroxy-*m*-tolyl methyl ether, dissolved in ice-cold aqueous alcohol, is oxidised by ferric chloride to 5:5'-dimethoxy-3:3'-dimethyl-4:4'-diphenoquinone (annexed formula), dark violet needles, m. p. 202—203°, which is reduced by zinc dust and acetic acid to 4:4'-dihydroxy-5:5'-dimethoxy-3:3'-dimethyldiphenyl, colourless crystals, m. p. 188.5—189.5°, which are



reconverted into the quinone by ferric chloride. The quinol is demethylated by hydrobromic acid (D 1.48) at 150°, thereby giving 4:5:4':5'-tetrahydroxy-3:3'-dimethyldiphenyl, m. p. 230—231° (decomp.) after darkening from 220° (*tetra-acetate*, needles, m. p. 193.5—194.5°). 4:4':5:5'-Tetramethoxy-3:3'-dimethyldiphenyl forms leaflets, m. p. 102—103°.

2:3-Dihydroxytoluene is oxidised by ferric chloride in aqueous



solution to the *substance* (annexed formula), bluish-black precipitate; a suitable method of purifying the compound could not be discovered, and its constitution is deduced in part from its analysis, in part from its reduction to a colourless material, which is converted by acetic anhydride into 4:5:4':5'-tetra-acetoxy-3:3'-dimethyldiphenyl. Under similar conditions, hydrourushiol is transformed by ferric

chloride into a *substance*,  $(C_{42}H_{67}O_4)_2Fe$ , bluish-black precipitate, whilst hydrourushiol monomethyl ether gives a reddish-brown, crystalline *precipitate*,  $C_{15}H_{31} \cdot C_6H_2O(OMe) \cdot C_6H_2O(OMe) \cdot C_{15}H_{31}$ , m. p. 120—122°, which is reduced by zinc dust and acetic acid to the colourless *phenol*,

$C_{15}H_{31} \cdot C_6H_2(OMe)(OH) \cdot C_6H_2(OH)(OMe) \cdot C_{15}H_{31}$ , m. p. 80—81.5°.

An alcoholic solution of 2-hydroxy-*m*-tolyl methyl ether is oxidised by air in the presence of laccase to 5:5'-dimethoxy-3:3'-dimethyl-4:4'-diphenoquinone; an aqueous solution of 2:3-dihydroxytoluene is only slightly affected by air, but, in the presence of laccase, a brown precipitate forms slowly which does not melt below 280°.

H. W.

**Phenyl-*o*-tolyltellurium Compounds.** KARL LEDERER (*Ber.*, 1920, 53, [B], 1674—1680. Compare this vol., i, 482, and earlier abstracts).—The action of Grignard's reagents on diaryltelluronium dihaloids leads to the formation of triaryltelluronium salts, which are reduced by an excess of the reagent to tellurides. The latter reaction can occur in three directions, giving (i) a simple telluride,  $TeR_2R' \cdot Hal. + R' \cdot MgHal. = TeR_2 + R'_2 + MgHal_2$  (this type of

change is frequently observed with magnesium methyl iodide); (ii) a mixed telluride,  $\text{TeR}_2\text{R}'\cdot\text{Hal.} + \text{R}'\cdot\text{MgHal.} = \text{R}\cdot\text{TeR}' + \text{R}\cdot\text{R}' + \text{MgHal.}_2$ ; or (iii) a mixture of the two possible products. The last type is now exemplified in the action of magnesium phenyl bromide on di-*o*-tolyltelluronium dibromide, or of *o*-tolylmagnesium bromide on diphenyltelluronium dibromide, which leads to the formation of a mixture of simple and mixed tellurides, and thus forms a contrast with the action of magnesium phenyl bromide on di-*p*-tolyltelluronium dibromide, which leads solely to the production of phenyl *p*-tolyl telluride. The mixture of tellurides is converted into the corresponding dibromides, which are separated by fractional crystallisation, and the individual dibromides are subsequently reduced to the corresponding tellurides by magnesium methyl iodide.

*Phenyl o-tolyl telluride*,  $\text{TePh}\cdot\text{C}_6\text{H}_4\text{Me}$ , is a pale orange-yellow oil, b. p.  $212\text{--}213^\circ/22\text{ mm.}$  It yields the following derivatives: *dibromide*, microscopic, six-sided platelets or monoclinic rods, m. p.  $154\text{--}155^\circ$  after softening at  $150\text{--}151^\circ$ ; *dichloride*, four-sided rods and hexagonal platelets, m. p.  $179\text{--}180^\circ$  after softening at  $176^\circ$ ; *di-iodide*, red, monoclinic crystals, m. p.  $172\text{--}173^\circ$  after sintering at about  $169^\circ$ ; *oxide*, colourless prisms, which soften at  $214^\circ$  and have m. p.  $216\text{--}217^\circ$  to a turbid liquid, which becomes transparent at  $218^\circ$ ; *mercuri-iodide*,  $\text{TePh}\cdot\text{C}_6\text{H}_4\text{Me}, \text{HgI}_2$ , small, yellow needles, m. p.  $133\text{--}134^\circ$  after softening at about  $123^\circ$ . *Phenyl-o-tolylmethyltelluronium iodide*, needles, m. p.  $119\text{--}120^\circ$  (decomp.) after softening at  $116\text{--}117^\circ$ , is generally a stable substance, which appears suitable for the preparation of optically active tellurium compounds.

H. W.

**The Stability of Solutions of Benzyl Alcohol.** DAVID I. MACHT and ALFRED T. SHOHL (*J. Pharm. expt. Ther.*, 1920, **16**, 61—69).—Solutions of benzyl alcohol kept in non-soluble glass vessels preserve their anæsthetic properties completely for long periods of time, and such solutions tend to increase their hydrogen-ion concentration very slowly.

When kept in soft glass containers, the fluid tends to become alkaline, and the drug rapidly deteriorates in anæsthetic efficiency.

J. C. D.

**Preparation of Benzyl Esters and other Benzyl Derivatives from Benzyl Chloride.** M. GOMBERG and C. C. BUCHLER (*J. Amer. Chem. Soc.*, 1920, **42**, 2059—2072).—Benzyl chloride, when heated with the dry salts of various organic acids in the presence of copper as a catalyst, gives fair yields of the corresponding esters. Much higher yields of purer esters are obtained by simply heating benzyl chloride and aqueous solutions of the salts, the mixture being thoroughly stirred all the time. Similarly with aqueous solutions of sodium phenoxides, benzyl chloride gives fair yields of mixtures of benzyl ethers and benzylphenols, the relative proportions of the two products varying with the phenol

used. Good yields of the mixed mono-, di-, and tri-benzylamines were obtained from benzyl chloride and aqueous solutions of ammonium carbonate. The relative proportions of primary, secondary, and tertiary amines varied according to the proportions of the reacting substances. Equally good results were obtained when the ammonium carbonate was replaced by aniline, methylaniline, or *m*- or *p*-toluidine. For the preparation of benzyl cyanide from the chloride and sodium cyanide, it is quite satisfactory to use water as the solvent.

In the preparation of benzyl alcohol by hydrolysis of the chloride, it is preferable to use sodium hydroxide rather than the carbonate, and to keep the time of boiling as short as possible.

W. G.

**Interaction between Ester and Alcohol Groups in the Presence of Catalysts.** EMIL FISCHER [with ERNST PFÄHLER and FRITZ BRAUNS] (*Ber.*, 1920, **53**, [B], 1634—1644).—Glycerol  $\alpha$ -benzoate is moderately rapidly converted in ethereal solution in the presence of potassium carbonate into a mixture of glycerol and dibenzoin. The process is more conveniently followed with the benzoyl derivatives of ethylene glycol in chloroform solution, whereby it is shown that the change is balanced and attains an equilibrium in the presence of the glycol and the mono- and di-benzoates. Similar phenomena are observed with the esters of monobasic acids. The action of the potassium carbonate appears to be definitely catalytic, since very small amounts of it are sufficient to accelerate the change. The phenomena are strikingly similar to those observed by Purdie (*T.*, 1887, **53**, 391), who found that an exchange of alkyl radicles readily took place between simple esters and alcohols in the presence of a small amount of sodium alkyloxide. It is considered possible that similar displacements may occur among the esters of polyhydroxy-alcohols in the absence of catalysts and at the ordinary temperature, and that herein may be the explanation of the gradual change in melting point observed by Grün to take place when diacyl derivatives of glycerol are preserved, and also of the so-called "ageing" of the natural fats.

The monobenzoate of ethylene glycol, when preserved during twenty-four hours in boiling chloroform solution in contact with anhydrous potassium carbonate, yields a considerable proportion of ethylene dibenzoate, whilst a mixture of molar quantities of the latter and ethylene glycol under similar conditions yields unchanged materials and the monobenzoate. Similarly, ethylene dibenzoate and ethyl alcohol yield ethyl benzoate and the mono- and di-benzoates of ethylene glycol, whilst ethylene glycol and methyl benzoate give unchanged ester and the mono- and di-benzoates of ethylene glycol. Resorcinol monobenzoate becomes decomposed into the dibenzoate and resorcinol, and, conversely, can be obtained from these substances. Glycerol monoacetate is largely transformed into diacetin. Glycerol and methyl benzoate, when heated with sodium methoxide in pyridine-methyl-alcoholic solution, yield glycerol

benzoates. Similarly, glycerol and methyl salicylate give glycerol salicylates. *iso*Propylideneglycerol and methyl benzoate under similar conditions are partly converted into *isopropylideneglycerol* benzoate, whilst tribenzoin and glycerol give a mixture of glycerol mono- and di-benzoates. Methyl benzoate and benzyl acetate are partly transformed into methyl acetate and benzyl benzoate in chloroform solution in the presence of sodium methoxide, or in methyl-alcoholic sodium methoxide solution.

The following substances have been incidentally prepared during the course of the investigation: *trimethylene glycol monobenzoate*, colourless, relatively mobile oil, b. p. 163—164°/12 mm.,  $D_4^{145}$  1.141, and dibenzoate, m. p. 59°, from trimethylene glycol and benzoyl chloride in the presence of quinoline; *trimethylene glycol di-p-nitrobenzoate*, long, shining needles, m. p. 120° (corr.) after slight previous softening; *trimethylene glycol mono-p-nitrobenzoate*, long needles arranged in clusters, m. p. 49°. H. W.

#### Melting Point of Acetylsalicylic [*o*-Acetoxybenzoic] Acid.

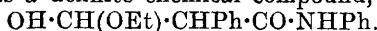
G. CAPPELLI (*Giorn. Chim. Ind. Appl.*, 1920, **2**, 291—300).—The melting point of aspirin, determined in a capillary tube, is 132° if incipient fusion is taken, or 135° for complete transparency. [See also Dahm, A., 1919, i, 124.] T. H. P.

#### Isomerism of Formylphenylacetic Esters. V. Anilides and Piperidides of Formylphenylacetic Acid.

WILHELM WISLICENUS and RUDOLF ERBE (*Annalen*, 1920, **421**, 119—158).—In continuation of previous work (compare A., 1917, i, 268), the anilides and piperidides of formylphenylacetic acid have now been investigated. In each case, two forms have been isolated, which, according to the evidence of the ferric chloride reaction and the Meyer bromine titration method, are to be regarded as enols, and hence also as geometrical isomerides, although it has not yet been found possible to assign a definite structure to each form. The definite enolic behaviour exhibited by each pair of isomerides appears to render the position of the corresponding esters the more remarkable, and, in this connexion, the authors are not prepared to admit the validity of the arguments advanced by Dieckmann (A., 1918, i, 15). The additive capacity, which has already been observed to some extent with the methyl and ethyl esters (*loc. cit.*), is more marked with the anilides and piperidides, which give stable compounds with methyl and ethyl alcohols, and, in the latter instance, with water also.

Formic ester is slowly added to an ice-cold solution and suspension of phenylacetanilide in dry ether in the presence of sodium wire, when the sodium derivative gradually separates. The instability of the latter towards water prohibits the use of the selective acidification method of obtaining the  $\alpha$ - or  $\beta$ -anilides, and the product is therefore treated with water and immediately run into an excess of dilute ice-cold sulphuric acid, the crude product consisting mainly of the  $\beta$ -anilide.  *$\alpha$ -Formylphenylacetanilide*,

$\text{OH}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CO}\cdot\text{NHPh}$ , colourless, six-sided plates, is prepared in the pure condition by recrystallisation of the crude product from benzene (whereby it is necessary to work rapidly) or, less advantageously, from boiling light petroleum. It has m. p.  $68^\circ$ , and, when further heated, resolidifies, and again melts at  $98^\circ$ . In alcoholic solution it gives an immediate dark violet coloration with ferric chloride. It is slowly transformed at the ordinary temperature into the  $\beta$ -modification (more rapidly when heated) or when preserved in contact with less benzene than is requisite for complete solution (the dissolved portion, however, consists exclusively of the  $\alpha$ -variety).  $\beta$ -Formylphenylacetanilide is isolated as described above or by crystallisation of the crude product from ether or glacial acetic acid. It forms colourless, three-sided leaflets, m. p.  $98^\circ$  (occasionally higher), is stable in absence of air, but is slowly oxidised by the latter to a viscous, yellow syrup, and, in alcoholic solution, gives an immediate, intense violet coloration with ferric chloride. Either variety gives an additive compound with ethyl alcohol, slender needles, m. p.  $104\text{--}106^\circ$  (decomp.), which slowly loses alcohol when preserved; the relative stability of the substance, its inability to develop an immediate coloration with ferric chloride, and its failure to decolorise bromine cause it to be regarded as a definite chemical compound,



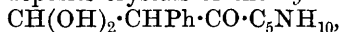
The corresponding product from methyl alcohol, silky needles, m. p.  $107\text{--}108^\circ$  (gas evolution), is considerably more stable, and can be preserved unchanged if air is excluded; on exposure to air, it slowly eliminates formic acid. When titrated with bromine in alcoholic solution, the  $\alpha$ - and  $\beta$ -forms indicate the presence of 96.5% and 98.8% of enol respectively.

The following metallic derivatives of formylphenylacetanilide are described: *sodium* compound, yellowish-white, somewhat unstable, crystalline precipitate, which could not be completely purified; *copper* compound, dark green, microscopic, silky needles, m. p.  $172\text{--}173^\circ$  (from alcohol), or prisms ( $+ \text{C}_6\text{H}_6$ ) from benzene; *iron* compound, slender, red needles, m. p.  $207\text{--}209^\circ$ .

Formylphenylacetanilide is converted at  $120\text{--}140^\circ$  into  $\beta$ -anilino- $\alpha$ -phenylacrylanilide,  $\text{NHPh}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CO}\cdot\text{NHPh}$ , yellow, hexagonal plates or almost colourless needles, m. p.  $106\text{--}107^\circ$ , and diphenylcarbamide and phenylacetaldehyde; the former substance is much more smoothly produced by the action of an excess of aniline on formylphenylacetanilide at  $60^\circ$ . With phenylhydrazine, the anilide gives the corresponding *phenylhydrazone*, slender, colourless needles, m. p.  $170\text{--}171^\circ$ , which, at  $200\text{--}220^\circ$ , loses aniline and forms 1:4-diphenylpyrazolone, needles, m. p.  $194\text{--}195^\circ$ . In one instance, an *additive* compound, small, colourless needles, m. p.  $158\text{--}160^\circ$ , was isolated from formylphenylacetanilide and phenylcarbimide, but, in general, for some unexplained reason, the action of the substances results in the evolution of carbon dioxide and production of  $\beta$ -anilino- $\alpha$ -phenylacrylanilide, m. p.  $106\text{--}108^\circ$ . Saturated alcoholic hydrogen chloride, or, pre-

ferably, concentrated sulphuric acid, converts  $\alpha$ - or  $\beta$ -formylphenylacetanilide into  $\beta$ -phenyl- $\alpha$ -carbostyryl, colourless needles, m. p. 227—228°. Either form of the anilide (or the corresponding alcoholates) suffers autoxidation on exposure to air, yielding formic acid and benzoylformanilide, m. p. 63—64°, the latter being, however, more smoothly obtained from the anilides by oxidation with potassium permanganate in acetone solution.

*Piperidine phenylacetate*, long, slender needles, m. p. 101—103°, is converted at 180—200° into *phenylacetopiperidide*, colourless needles, m. p. 5—7°, b. p. 200—203°/12 mm. (which is conveniently purified through the *hydrochloride*, needles, m. p. 84—86°). The piperidide condenses with ethyl formate in ethereal solution in the presence of metallic sodium, yielding *sodium formylphenylacetopiperidide*, colourless, crystalline powder, which could not be completely purified; when suddenly acidified by an excess of cold dilute sulphuric acid, the sodium derivative yields formylphenylacetopiperidide, m. p. 110—116°, which is probably to be regarded as the crude  $\beta$ -form. After being crystallised from a mixture of benzene and light petroleum, it gives  *$\alpha$ -formylphenylacetopiperidide*,  $\text{HO}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CO}\cdot\text{C}_5\text{NH}_{10}$ , indistinct, colourless, microscopic crystals, m. p. 104—106°, which becomes oxidised, with evolution of formic acid, on exposure to air, and yields an immediate violet coloration with ferric chloride. In contrast to the crude product, the pure  $\alpha$ -form is soluble in cold water, and the solution gradually deposits crystals of the *hydrate*,



m. p. 114° (the same substance is obtained when carbon dioxide is passed into an aqueous solution of sodium formylphenylacetopiperidide); the substance is remarkably stable, and does not give an immediate coloration with ferric chloride. When heated in a vacuum at 70—80°, it loses the theoretical quantity of water, leaving a residue, m. p. 122°, which gives a violet coloration with ferric chloride (?  $\beta$ -formylphenylacetopiperidide), but, after repeated crystallisation from benzene and light petroleum, has m. p. 104—106° ( $\alpha$ -form). The hydrate is transformed by boiling methyl alcohol into the corresponding *methyl alcoholate*, colourless plates, m. p. 116—117°, and by ethyl alcohol into the *ethyl alcoholate*, microscopic platelets or long prisms, m. p. 98°. *Formylphenylacetopiperididephenylhydrazone* crystallises in colourless, rectangular plates, m. p. 158—159°, which gradually decompose when preserved, and is transformed at 180—200° into piperidine and 1:4-diphenylpyrazolone, m. p. 195—196°.

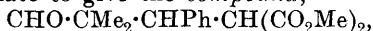
Phenylacetodiphenylamide,  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NPh}_2$ , m. p. 73—74° (Hausknecht gives 72°), is conveniently prepared from phenylacetyl chloride and diphenylamine in the presence of pyridine; when treated with ethyl formate and potassium ethoxide in alcoholic-etheral solution, it is quantitatively converted into diphenylamine and ethyl formylphenylacetate. A similar result was obtained when metallic sodium and ether were employed, the reaction in this instance occurring very slowly.

H. W.

**Addition of Aliphatic Aldehydes to Unsaturated Compounds. New Synthesis of  $\delta$ -Lactones.** HANS MEERWEIN (*Ber.*, 1920, **53**, [B], 1829—1835).—In continuation of previous work (A., 1919, i, 21), it is shown that aliphatic aldehydes which contain at least one hydrogen atom attached to the carbon atom vicinal to the aldehyde group are pre-eminently capable of condensing with unsaturated aldehydes and ketones, with the formation of dialdehydes or ketonic aldehydes. The additive capacity probably depends on the desmotropic character of the aldehydes; attempts to isolate sodium derivatives by the action of sodium, sodium alkoxide, or sodamide on ethereal solutions of the aldehydes were not, however, successful, since the corresponding aldols were immediately produced, even at  $-40^\circ$ . In connexion with the latter observation, it is somewhat surprising that potassium methoxide can be used as condensing agent with aldehydes, but the explanation is found in the fact that aldol formation occurs much more slowly in alcoholic solution than in any other solvent, owing to the reversible production of hemiacetals,  $\text{OH}\cdot\text{CHR}\cdot\text{OR}'$ .

The  $\alpha\epsilon$ -dialdehydes and  $\alpha\epsilon$ -ketoaldehydes are smoothly converted into the isomeric  $\delta$ -lactones by an intramolecular Cannizzaro reaction under the influence of alcoholic alkoxide. The isolation of the dialdehydes or ketoaldehydes in the pure condition is quite unnecessary for this purpose, since by suitable modification of temperature, period of heating, and concentration of alkali it is possible to obtain either the primary product, the  $\delta$ -lactone, or the corresponding hydroxy-acid.

The additive capacity of aliphatic aldehydes also extends to  $\alpha\beta$ -unsaturated esters; thus, *isobutaldehyde* combines with methyl benzyldenemalonate to give the compound,



m. p.  $150$ — $152^\circ$ , and this points the way to a possible simple synthesis of  $\delta$ -aldehyde-acids.

Finally,  $\alpha\beta$ -unsaturated aldehydes, which contain at least one hydrogen atom attached to the carbon atom vicinal to the double bond, readily condense with other unsaturated substances; thus,  $\alpha$ -methyl- $\beta$ -ethylacraldehyde unites with phenyl styryl ketone, yielding the compound,  $\text{CH}_2\text{Bz}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{CH}:\text{CMe}\cdot\text{CHO}$ . The last reaction explains the transformations suffered by acetophenone when heated with sodium ethoxide; in all cases, the primary product is dypnone,  $\text{COPh}\cdot\text{CH}:\text{CMePh}$ , which, as an  $\alpha\beta$ -unsaturated ketone, readily unites with other unsaturated compounds, thus yielding dypnopinacone,  $\text{CHBz}\cdot\text{CPh}\cdot\text{CH}_2\cdot\text{CMePh}\cdot\text{CH}_2\text{Bz}$ , and the compound,  $\begin{array}{c} \text{CPh}\cdot\text{CH}:\text{CPh} \\ \text{CBz}\cdot\text{CMe}\cdot\text{CH} \end{array}$ , described by Castaldi (this vol., i, 391).

[With GEORG KILLING].— $\gamma$ -Benzoyl- $\beta$ -phenyl- $\alpha\alpha$ -dimethyl-*n*-butaldehyde,  $\text{CH}_2\text{Bz}\cdot\text{CHPh}\cdot\text{CMe}_2\cdot\text{CHO}$ , needles, m. p.  $105$ — $106^\circ$ , which decomposes when further heated into its components, is prepared by warming a methyl-alcoholic solution of phenyl styryl ketone and *isobutaldehyde* with a solution of potassium methoxide at  $40^\circ$ ; the aldehyde is oxidised by chromic acid to  $\gamma$ -benzoyl- $\beta$ -

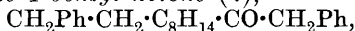
phenyl- $\alpha\alpha$ -dimethyl-*n*-butyric acid, m. p. 160°. If the reaction mixture is allowed to remain in contact with a further quantity of potassium methoxide, the corresponding lactone is obtained, which, however, is somewhat difficult to isolate, so that it is preferable to convert it first into  $\delta$ -hydroxy- $\beta\delta$ -diphenyl- $\alpha\alpha$ -dimethyl-*n*-valeric acid,  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ , rhombic prisms, m. p. 154—155°, from dilute acetic acid, prismatic plates (+  $\text{CHCl}_3$ ) from chloroform, which yields the lactone, coarse needles, m. p. 106—107°, when heated at 200°.

[With KARL STEINACKER.]— $\alpha\gamma\gamma$ -Trimethyl- $\beta$ -ethyl- $\delta$ -valerolactone,  $\begin{array}{c} \text{CHEt}\cdot\text{CHMe}\cdot\text{CO} \\ | \quad | \\ \text{CMe}_2-\text{CH}_2-\text{O} \end{array}$ , almost colourless, mobile oil, b. p. 140°/17—18 mm.,  $D_4^{20}$  0.892,  $n_D^{20}$  1.46412, is obtained from isobutaldehyde and  $\alpha$ -methyl- $\beta$ -ethylacraldehyde; the corresponding hydroxy-acid is unstable in the free state, and is oxidised by potassium permanganate to  $\alpha\alpha\gamma$ -trimethyl- $\beta$ -ethylglutaric acid,  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CHEt}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , small, prismatic crystals, m. p. 135—136°. H. W.

**Reactions with  $\alpha$ -Campholide and Ethyl Bromocampholate.** H. RUPE and A. JÄGGI (*Helv. Chim. Acta*, 1920, 3, 654—668).— $\alpha$ -Campholide may be obtained in almost theoretical yield by heating camphoric anhydride in contact with a nickel catalyst and in a current of hydrogen, using an electric furnace, as previously described (A., 1919, i, 29, 334). When the temperature of the furnace is too high and the current of hydrogen insufficient, the campholide formed is accompanied by volatile oils, consisting partly of oxygenated compounds and partly of unsaturated hydrocarbons of the formula  $\text{C}_9\text{H}_{16}$ .

By a slight modification of Baeyer and Villiger's method of preparation (A., 1900, i, 133), bromocampholic acid may be obtained in 80% yield; the acid crystallises in plates or leaflets, m. p. 177° (decomp.). The following derivatives of the acid have been prepared. The *chloride*,  $\text{C}_{10}\text{H}_{16}\text{OClBr}$ , best obtained with the help of thionyl chloride, forms stout crystals of monoclinic habit, m. p. 57.5°; the *amide*,  $\text{C}_{10}\text{H}_{18}\text{ONBr}$ , fine needles, m. p. 207°; the *anilide*,  $\text{CH}_2\text{Br}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}\cdot\text{NHPh}$ , white needles, m. p. 142°; the *phenylhydrazide*,  $\text{CH}_2\text{Br}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$ , slender needles, m. p. 150—151°; the *methyl ester*, colourless, greasy oil, b. p. 139°/15 mm.; the *ethyl ester*, m. p. 9—10°, b. p. 142—143°/13 mm.; the *phenyl ester*, colourless plates, m. p. 46—47°, b. p. 204°/11 mm.

A compound,  $\text{C}_{24}\text{H}_{30}\text{O}$ , which may be 3-phenylethyl-1:2:2-trimethylcyclopentane 1-benzyl ketone (?),



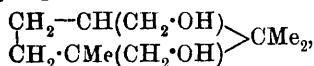
obtained in small yield by the interaction of ethyl bromocampholate and magnesium benzyl chloride, forms large, shining leaflets, m. p. 119°, b. p. 245—250°/14 mm.

When heated with quinoline, aniline, or dimethylaniline, ethyl bromocampholate loses ethyl bromide, giving  $\alpha$ -campholide. When heated with methyl-alcoholic potassium hydroxide, however, it loses



only hydrogen bromide, yielding *ethyl 1:2:2-trimethyl-3-methylenecyclopentane-1-carboxylate*,  $\text{CH}_2\cdot\text{C}_8\text{H}_{13}\cdot\text{CO}_2\text{Et}$ , which is a colourless oil of pleasant, aromatic odour, b. p.  $93^\circ/12\text{ mm.}$ ,  $[\alpha]_D^{20} + 20\cdot62^\circ$  ( $12\cdot99^\circ$ ),  $[\alpha]_D^{20} + 26\cdot73^\circ$  ( $16\cdot38^\circ$ ),  $[\alpha]_{\text{H}_2\text{O}}^{20} + 31\cdot57^\circ$  ( $18\cdot97^\circ$ ),  $[\alpha]_F^{20} 41\cdot24^\circ$  ( $25\cdot41^\circ$ ) (the values in brackets being for its solution in benzene),  $n_D 1\cdot45575$ ,  $n_D 1\cdot45773$ ,  $n_B 1\cdot46446$ ,  $n_\gamma 1\cdot47005$ ; when treated with bromine in chloroform, this unsaturated ester yields its *bromo-derivative*,  $\text{C}_{12}\text{H}_{19}\text{O}_2\text{Br}$ , m. p.  $149^\circ$ .

*1:2:2-Trimethylcyclopentane-1:3-dimethanol*,



obtained by reducing  $\alpha$ -campholide with sodium and alcohol, forms long, shining needles, m. p.  $130^\circ$ , b. p.  $151\text{--}154^\circ/12\text{ mm.}$

$\alpha$ -Camphidone (compare Oddo and Leonardi, A., 1897, i, 86; Tafel and Eckstein, A., 1902, i, 43; Rupe and Splittgerber, A., 1907, i, 1016; Tafel and Bubnitz, A., 1906, i, 43) may be prepared in good yield by heating  $\alpha$ -campholide in a sealed tube with zinc chloride and ammonia, and camphidine (Tafel and Eckstein, *loc. cit.*) may be obtained by similar treatment of the above glycol.

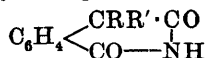
T. H. P.

**The Vapour Pressure of Phthalic Anhydride.** K. P. MONROE (*J. Ind. Eng. Chem.*, 1920, 12, 969—971. Compare this vol., i, 164).—The vapour pressure of phthalic anhydride at various temperatures was found to be as follows:

$t$ .....	$212\cdot0^\circ$	$222\cdot0^\circ$	$234\cdot6^\circ$	$241\cdot5^\circ$	$252\cdot4^\circ$	$284\cdot6^\circ$
$p$ (mm. Hg)	130·5	172·1	241·2	287·1	369·4	759·3

The interpolation formula applicable to these data is:  $\log_{10} p = 7\cdot94234 - 2823\cdot5/T$ , where  $p$  is the vapour pressure in mm. of mercury and  $T$  the absolute temperature. W. P. S.

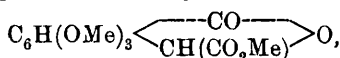
**A New Class of Hypnotics. The Dialkylhomophthalimides.** AUGUSTE LUMIÈRE and FÉLIX PERRIN (*Compt. rend.*, 1920, 171, 637—639).—Dialkylhomophthalimides of the type



may readily be obtained by the action of the corresponding alkyl iodides on homophthalimide in the presence of sodium ethoxide. The following have been prepared: *diethylhomophthalimide*, m. p.  $144^\circ$ ; *ethylpropylhomophthalimide*, m. p.  $117^\circ$ ; *dipropylhomophthalimide*, m. p.  $128^\circ$ ; *dialkylhomophthalimide*, m. p.  $140\text{--}141^\circ$ . All these compounds are hypnotics, whilst, at the same time, their toxicity is very slight, and they are apparently free from any unfavourable secondary action. W. G.

**Some Derivatives of Phthalide.** J. HERZIG [with HEDWIG BRUNNER and MARIANNE SCHLEIFFER] (*Annalen*, 1920, 421, 283—292).—In connexion with the work on gallicflavin (this vol.,

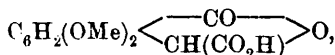
i, 863), it has been found necessary to repeat the investigations of Bargellini and Molina (A., 1912, i, 773) on 3:4:5-trimethoxyphthalide. The preparation of 3:4:5-trimethoxytrichloromethylphthalide,  $C_6H(OMe)_3 \langle \begin{smallmatrix} CO \\ CH(CCl_3) \end{smallmatrix} \rangle O$ , by the action of chloral on methyl trimethylgallate, could not be satisfactorily repeated, but by hydrolysis of the crude product of the action, followed by treatment with diazomethane, it was found possible to isolate *methyl 3:4:5-trimethoxyphthalidecarboxylate*,



monoclinic crystals,  $a:b:c=1.1366:1.06983$ ,  $\beta=122^\circ 33'$ , m. p.  $119-121^\circ$ , in reasonable yield, which is hydrolysed by methylalcoholic potassium hydroxide to 3:4:5-trimethoxycarboxyphthalide, m. p.  $146-149^\circ$  (Bargellini and Molina give m. p.  $142-143^\circ$ ). Distillation under diminished pressure or treatment with sodium acetate and acetic anhydride (but not with the latter alone) transforms the acid quantitatively into 3:4:5-trimethoxyphthalide, monoclinic crystals,  $a:b:c=0.9548:1.09640$ , m. p.  $133-135^\circ$  (Bargellini and Molina, m. p.  $134-135^\circ$ ).

The melting point of 3:4:5-trimethoxy-*o*-phthalic acid has been recorded as  $175-176^\circ$  by Windaus (A., 1911, i, 904),  $174^\circ$  by Bargellini and Molina (*loc. cit.*), and still higher by Feist (A., 1908, i, 100); a specimen prepared by the oxidation of 3:4:5-trimethoxyphthalide had the constant m. p.  $145-148^\circ$  (decomp.), and readily yielded the corresponding *methyl* ester, m. p.  $62-65^\circ$ . A specimen prepared by the authors, and subsequently recrystallised three times from a mixture of ether and light petroleum by Windaus, had m. p.  $171^\circ$  after some previous softening. Apparently, the conversion of the acid into the anhydride is greatly catalysed by traces of impurity, possibly derived from the alkali of the glass capillaries.

Methyl 2:3-dimethoxybenzoate condenses with chloral hydrate in the presence of concentrated sulphuric acid, with the formation of 5:6-dimethoxytrichloromethylphthalide, m. p.  $105-107^\circ$  (Fritsch, A., 1898, i, 663, gives  $104^\circ$ ), which is hydrolysed with some difficulty to 5:6-dimethoxycarboxyphthalide,



m. p.  $151-154^\circ$ . The latter is quantitatively transformed into 5:6-dimethoxyphthalide, m. p.  $99-101^\circ$ , when distilled under diminished pressure. No evidence of the formation of Fritsch's 2-carboxy-3:4-dimethoxymandelic acid could be observed.

H. W.

**The Bile Acids. VI.** MARTIN SCHENCK (*Zeitsch. physiol. Chem.*, 1919, 107, 152-156).—Cilanic acid and hydroxylamine hydrochloride were dissolved in 10% sodium hydroxide, and, after heating in steam for a few hours, the mixture was left for twenty-

four to forty-eight hours at the ordinary temperature. On the addition of dilute hydrochloric acid, a pasty precipitate was formed. The precipitate, as well as the filtrate, was extracted with ether, and the ethereal extract evaporated at the ordinary temperature, and eventually in a vacuum. A white, amorphous substance was thus obtained, which gave Lassaigne's reaction. This substance was extracted twice with ether (fractions *A* and *B*), leaving a residue fraction, *C*. The three fractions commenced liquefying at about 100° and frothing about 120—125°, after which temperature they decomposed. The nitrogen analyses of all three fractions agreed with the figures for the *oxime* of cilianic acid,  $C_{24}H_{34}O_9 \cdot NOH$ , in which only one ketone group reacts with the hydroxylamine. The theory of the formation of cilianic acid from bilianic acid, and its bearing on the other inactive ketone group, is discussed.

S. S. Z.

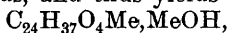
**Unsaturated Bile Acids.** FR. BOEDECKER (*Ber.*, 1920, 53, [*B*]. 1852—1862).—The only unsaturated bile acids which have been isolated previously are cholatrienecarboxylic acid (Wieland and Weil, A., 1912, i, 830) and choladienecarboxylic acid (Wieland and Sorge, A., 1917, i, 685), which are obtained from cholic and deoxycholic acids, respectively, by distillation under diminished pressure, and in which the hydroxyl groups of the parent acids are completely absent. The author has examined the behaviour of cholic acid towards milder dehydrating agents (molten glycollic acid and potassium hydrogen sulphate, dilute sulphuric acid, zinc chloride, oxalic acid, phosphoric acid), and has obtained products from which an unsaturated dihydroxy-bile acid,  $C_{24}H_{38}O_4$ , can be isolated in good yield, and for which he proposes the name *apocholic* acid. It follows that one of the three secondary hydroxy-groups of cholic acid is particularly readily eliminated under the action of dehydrating agents, whilst the remaining two are considerably more firmly retained. Now Borsche (A., 1919, i, 276) has shown that two hydroxyl groups are present in the same positions in the molecules of cholic and deoxycholic acid, and, if the third hydroxyl group of the former is the one which is lost, *apocholic* acid must be an unsaturated derivative of deoxycholic acid. The direct hydrogenation of *apocholic* to deoxycholic acid has not been effected up to the present, since the substance is peculiarly resistant to the action of hydrogen, but the two acids are so similar in their general chemical behaviour that they can readily be mistaken the one for the other.

Cholic acid is converted by zinc chloride in boiling acetic acid solution into a mixture of unchanged material, *apocholic acid* and less saturated acids; the latter are separated by treatment with cold ether, and are recovered from the ethereal solution as a pale yellow resin. Cholic and *apocholic* acids are separated by taking advantage of the sparing solubility of the former in cold alcohol, in which the latter dissolves readily. The crude *apocholic* acid is converted into its compound with acetic acid, and the latter

is crystallised from aqueous alcohol, the product being ultimately heated at  $120\text{--}130^\circ/0.1\text{--}0.3$  mm. *apoCholic acid* has m. p.  $173\text{--}174^\circ$ ,  $[\alpha]_D^{20} + 49.87^\circ$  in absolute alcoholic solution; it immediately decolorises alkaline potassium permanganate solution, readily absorbs bromine, with the formation of a *dibromide*, and gives a coloration with acetic anhydride and sulphuric acid similar to, but more decided than, that of deoxycholic acid. Its *alkali* salts are freely soluble in water, but the *calcium*, *barium*, and *strontium* salts are precipitated as plaster-like masses. The *magnesium* salt crystallises in very characteristic, slender needles; the *silver* salt was analysed. The following additive compounds are described: *acetic-apocholic acid*,  $C_{24}H_{38}O_4, C_2H_4O_2$ , small, colourless prisms, m. p.  $135\text{--}155^\circ$  after previous softening according to the manner of heating,  $[\alpha]_D^{20} + 45.35^\circ$  in alcoholic solution, which obstinately retains a portion of the acetic acid, even after protracted heating; *butyric-apocholic acid*,  $(C_{24}H_{38}O_4)_2, C_4H_8O_2$ , needles, m. p. about  $170^\circ$ ; *palmitic-apocholic acid*,  $(C_{24}H_{38}O_4)_3, C_{16}H_{32}O_2$ , slender needles, m. p.  $184\text{--}185^\circ$ ,  $[\alpha]_D^{20} + 43.7^\circ$  in absolute alcohol; *stearic-apocholic acid*, needles, m. p.  $185\text{--}186^\circ$ ; a compound could not be obtained with formic acid; with *benzene*, needles, m. p.  $174\text{--}175^\circ$ ; with *xylene*,  $(C_{24}H_{38}O_4)_2, C_8H_{10}$ , hexagonal plates, m. p.  $171\text{--}172^\circ$  after previous softening; with *naphthalene*,

$(C_{24}H_{38}O_4)_2, C_{10}H_8$ , slender needles, m. p.  $173\text{--}174^\circ$ ,  $[\alpha]_D^{20} + 41.20^\circ$  in absolute alcohol; with *ethyl alcohol*, slender needles, which lose alcohol on exposure to air; with *ethyl acetate* or *acetone*, unstable prisms; with *benzaldehyde*, needles, m. p.  $156^\circ$ ; with *d-camphor*,  $C_{24}H_{38}O_4, C_{10}H_{16}O$ , small needles, m. p.  $179\text{--}180^\circ$  after softening at  $177^\circ$ ,  $[\alpha]_D^{20} + 43.80^\circ$  in ethyl-alcoholic solution.

*Methyl apocholate* has m. p.  $88\text{--}90^\circ$  after slight previous softening; it retains a part of the ability of the parent acid to form additive compounds, and thus yields the *substances*,



long prisms, m. p.  $83\text{--}84^\circ$  after softening at  $75^\circ$ , which slowly loses methyl alcohol on exposure to air, and  $C_{24}H_{37}O_4Me, C_2H_4O_2$ , large prisms, m. p.  $87\text{--}88^\circ$  after slight softening at  $85^\circ$ .

H. W.

**The Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides. I. Some Derivatives of cyclopentene and dicyclopentane.** ERNEST HAROLD FARMER and CHRISTOPHER KELK INGOLD (T., 1920, 117, 1362—1373).

**The Resolution of the Keto-dilactone of Benzophenone-2 : 4 : 2' : 4'-tetracarboxylic Acid.** WILLIAM HOBSON MILLS and CHARLES REYNOLDS NODDER (T., 1920, 117, 1407—1410).

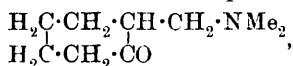
**Tannins. VI. Chebolic Acid. II.** KARL FREUDENBERG and BRUNO FICK (*Ber.*, 1920, 53, [B], 1728—1736. Compare A., 1919, i, 412).—Chebolic acid is decomposed by hot water into an amorphous acid and a crystalline tannin, which has been pro-

visionally regarded as a digalloylglucose. This hypothesis is now fully confirmed by observations on its degradation under the influence of tannase (compare this vol., i, 562); the increase in acidity and the relative proportions of gallic acid and dextrose can only be explained if the substance is regarded as a digalloylglucose, and this is confirmed by the results of the elementary analysis of the substance itself and of its crystalline *acetyl* derivative [di(triacetylgalloyl)-triacetylglucose, coarse needles, m. p. 177—179°], and of determinations of molecular weight, which can be effected in boiling acetone. The digalloylglucose is unaffected by emulsin, phaseolunataase, or yeast extract, and thus differs from the 1-galloyl- $\beta$ -glucose recently described by Fischer and Bergmann (A., 1919, i, 89). It is possibly a derivative of  $\alpha$ -glucose, but probably the 1-position of the sugar is free, and, in chebulinic acid, attached to the amorphous acid. Investigation of the latter is as yet incomplete. It does not crystallise in the free state. In addition to the thallium salt described previously (*loc. cit.*), the *brucine* salt, m. p. about 250° after darkening above 200°, has now been investigated. The composition of both these salts indicates that it is a dibasic acid,  $C_{14}H_{14}O_{11}$ , but it possibly contains a third, feebly acidic, group, since the equivalent, as determined by titration with litmus as indicator, corresponds with about  $\frac{1}{3}C_{14}H_{14}O_{11}$ . It yields pyrogallol when distilled under diminished pressure. The suggested formula,  $C_{14}H_{14}O_{11}$ , can be brought into harmony with the composition of chebulic acid if the latter is regarded as formed from digalloylglucose and the acid with the loss of two molecules of water:  $C_{20}H_{20}O_{14} + C_{14}H_{14}O_{11} = C_{34}H_{30}O_{23} + 2H_2O$ . Such a new formula for chebulic acid is in agreement with the most trustworthy analytical data recorded in the literature and with the molecular weight as determined by titration and by the ebullioscopic method with acetone as solvent. It also explains satisfactorily the observations recorded in the previous communication on the fission of chebulic acid.

It is, however, quite possible that the "fission acid" has only half the assumed molecular weight, although the composition of the salts does not harmonise so well for an acid such as  $C_7H_6O_6$ , and the explanation of the optical activity is difficult; in this case, two such molecules must be present in the molecule of chebulic acid. The hypothesis that the "fission acid" is actually a mixture, possibly of  $C_7H_6O_6$  and  $C_7H_8O_5$ , would explain many of its properties and be reconcilable with other observations, such as the ratio of the amounts of degradation products obtained from chebulic acid. Lastly, it is also possible that a third, readily detached gallic acid residue is present in chebulic acid. H. W.

**The Synthesis of  $\beta$ -Keto-bases from Amine Salts, Formaldehyde, and cycloHexanone.** C. MANNICH and R. BRAUN (*Ber.*, 1920, 53, [B], 1874—1880).—The synthesis, previously applied to aliphatic ketones (A., 1917, i, 634), has now been extended to cyclohexanone.

1-Dimethylaminomethylcyclohexan-2-one hydrochloride, colourless crystals, m. p.  $152^{\circ}$ , is readily obtained in 85% yield by the interaction of cyclohexanone in formaldehyde solution and dimethylamine hydrochloride. The corresponding free base,



has b. p. about  $100^{\circ}/13$  mm., and cannot be long preserved at the ordinary temperature; the *picrate*, pale yellow needles, m. p.  $149^{\circ}$ , *perchlorate*, m. p.  $156^{\circ}$ , and *aurichloride*, yellow prisms, m. p.  $132^{\circ}$ , are described. The *methiodide* is very unstable, decomposing at the ordinary temperature into trimethylammonium iodide and methylenecyclohexanone. The keto-base yields an *oxime hydrochloride*, very hygroscopic rods, m. p.  $158^{\circ}$ , and a *cyanohydrin*, broad needles, m. p.  $55^{\circ}$ ; it is oxidised to adipic acid by potassium permanganate or nitric acid. Reduction by means of aluminium amalgam and moist ether converts the ketone into 1-dimethylaminomethylcyclohexan-2-ol, colourless, stable oil, b. p.  $108^{\circ}/13$  mm. [the *hydrochloride*, very hygroscopic crystals, m. p.  $160^{\circ}$ , *picrate*, *acetate*, colourless liquid, b. p.  $136^{\circ}/13$  mm. (*hydrochloride*, m. p.  $141^{\circ}$ ), and *benzoate*, viscous oil (*hydrochloride*, needles, m. p.  $220^{\circ}$ ), are described].

The condensation of methylamine hydrochloride, formaldehyde, and cyclohexanone takes a more complicated course, but it has been found possible to isolate the following substances in the pure condition: (i) 1-methylenecyclohexan-2-one, b. p.  $65^{\circ}/13$  mm., *semicarbazone*, m. p.  $195^{\circ}$ ; (ii) the *ether*,  $\text{O}(\text{CH}_2\cdot\text{C}_6\text{H}_9\text{O})_2$ , rods, m. p.  $149^{\circ}$ , the constitution of which is deduced from its analysis, its inactivity towards acetic anhydride, and the formation of a *semicarbazone* and a *bisphenylhydrazone*, m. p.  $191^{\circ}$ ; and (iii) *biscyclohexanonylmethylmethylamine*,  $\text{MeN}\left[\begin{array}{c} \text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2 \\ \text{CO}-\text{CH}_2\cdot\text{CH}_2 \end{array}\right]_2$ , needles, m. p.  $172^{\circ}$  (the hygroscopic *hydrochloride*, *aurichloride*, *platinichloride*, *picrate*, yellow needles, m. p.  $175^{\circ}$ , and *methiodide*, quadratic crystals, m. p.  $144^{\circ}$ , are described).

Similarly, ammonium chloride, formaldehyde, and cyclohexanone give *tricyclohexanonylmethylamine*,  $\text{N}\left[\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2 \\ \text{CO}-\text{CH}_2\cdot\text{CH}_2 \end{array}\right]_3$ , slender crystals, m. p.  $119^{\circ}$ ; *hydrochloride*, coarse, colourless crystals, m. p.  $110^{\circ}$ .  
H. W.

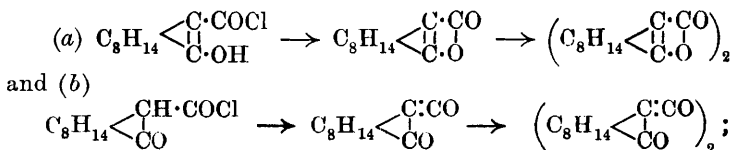
### Preparation of $\beta$ -Tetrahydronaphthyl Methyl Ketone.

ALBERT R. F. HESSE (*Ber.*, 1920, **53**, [B], 1645).—It has been observed by Scharwin (*A.*, 1902, i, 625) that acetyl chloride reacts unusually energetically with tetrahydronaphthalene, and that tetrahydronaphthyl methyl ketone can only be isolated in the pure state from the product by repeated fractional distillation. The difficulties attendant on the preparation have been ascribed by von Braun to the presence of dihydronaphthalene in the original material, and this suggestion appears to be confirmed by the

author's observation that pure tetrahydronaphthalene reacts slowly with acetyl chloride in carbon disulphide solution in the presence of aluminium chloride, with the production of  $\beta$ -tetrahydronaphthyl methyl ketone, b. p.  $182^\circ/20$  mm., which is obtained in the pure condition after a single distillation, and in almost 90% yield. The ketone is conveniently characterised as its *semicarbazone*, m. p.  $234-235^\circ$ . H. W.

**Relationships between the Dimeric Ketens and cyclo-Butane-1 : 3-dione and its Derivatives.** G. SCHROETER (*Ber.*, 1920, 53, [B], 1917—1926).—A reply to Staudinger's criticism (this vol., i, 517) on the author's conception of dimeric ketens as "polymolecules," in which the components are not united by main or subsidiary atomic valencies, but by molecular valencies (*A.*, 1917, i, 145).

The isolation of two camphorketens,  $\text{C}_8\text{H}_{14} \begin{smallmatrix} \diagup \\ \text{CO} \end{smallmatrix} \text{C} \begin{smallmatrix} \diagdown \\ \text{CO} \end{smallmatrix} \text{C} \begin{smallmatrix} \diagup \\ \text{CO} \end{smallmatrix} \text{C} \begin{smallmatrix} \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_8\text{H}_{14}$  and  $\text{C}_8\text{H}_{14} \begin{smallmatrix} \diagup \\ \text{CO} \end{smallmatrix} \text{C} \begin{smallmatrix} \diagdown \\ \text{CO} \end{smallmatrix} \text{C} \begin{smallmatrix} \diagup \\ \text{CO} \end{smallmatrix} \text{C} \begin{smallmatrix} \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_8\text{H}_{14}$ , has been considered by Staudinger as strong evidence in favour of regarding such substances as atomic compounds, but the author points out that the *cis-trans* nature of the isomerism has been by no means definitely established. The two forms differ most widely in their specific rotations in benzene and ethyl acetate solutions, and such considerable divergence is more readily explained by the assumption of structural isomerism, the greater specific rotation of the one isomeride being due to the presence in it of a double bond in close proximity to the asymmetric carbon atom. The argument is illustrated at the instance of methyl camphorcarboxylate, which, in the ketonic form, has  $[\alpha]_D + 18.40^\circ$  in benzene solution (mean value of a large number of determinations, in which  $c = 0.3-3.0$ ); in alcohol, ethyl acetate, acetone, ether, and chloroform, the values of  $[\alpha]_D^{20}$  are  $+59.58^\circ$ ,  $59.00^\circ$ ,  $54.39^\circ$ ,  $62.66^\circ$ , and  $62.33^\circ$ , respectively, and each of these solutions contains an equilibrium mixture. The completely enolised ester has  $[\alpha]_D^{20}$  about  $+154^\circ$  in benzene or alcohol, although this value is a little uncertain by reason of the unascertained influence of the sodium alkoxide added as enolising agent. It is certain, however, that the specific rotation of the enol is about eight times that of the ketone, and similar differences are recorded for other keto-enolic desmotropes in the camphor series. It appears therefore valid to conclude that Staudinger's camphorketens are keto-enolic isomerides, which may be regarded as formed from the desmotropic forms of camphorcarboxyl chloride in accordance with the schemes:



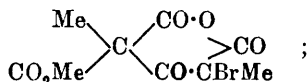
the form (a), which contains an olefinic double bond in close proximity to the two asymmetric carbon atoms, exhibits the higher optical activity.

The *cyclobutane*-1:3-diones cannot be considered as 1:3-*cyclobutenolones*, since they behave towards metals in indifferent media precisely as diketones, and are only attacked after addition of an enolising solvent, such as alcohol. Staudinger's explanation of the phenomena as due to passivity of the metal is insufficient, since the enolic forms react as strong acids. The author justifies his previous position with respect to the isomerism of the methylketencarboxylic esters,  $(\text{CO}_2\text{Me}\cdot\text{CMe}\cdot\text{CO})_2$ , and methyl 1:3-dimethyl*cyclobutanedionedicarboxylate*,

$$\text{CO}_2\text{Me} \begin{array}{c} \text{Me} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CO}_2\text{Me} \end{array} \begin{array}{c} \text{CO} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CO} \end{array} \begin{array}{c} \text{Me} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CO}_2\text{Me} \end{array}$$
and finds in the action of bromine (giving an additive product, which spontaneously eliminates methyl bromide) further evidence in favour of his mode of formulating the latter substance, since the reaction is readily explained by the intermediate formation of the product

$$\text{CO}_2\text{Me} \begin{array}{c} \text{Me} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CO}_2\text{Me} \end{array} \begin{array}{c} \text{COBr} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CO} \end{array} \text{CBr} \begin{array}{c} \text{CO}_2\text{Me} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{Me} \end{array}$$

which subsequently passes into the more stable anhydride,



the reaction is thus precisely analogous to the transformation, recorded by Staudinger, of the methyl ester of camphoryl chloride into a brominated camphoric anhydride under the influence of bromine at a low temperature.

The transformation of dimeric ketens into ketones and derivatives of  $\beta$ -ketocarboxylic acids cannot be regarded as evidence of their constitution, since they are readily depolymerised to the highly reactive simple ketens, which can readily unite with carboxylic acids or their derivatives to  $\beta$ -keto-acids. Further, the reverse transition of a true *cyclobutane*-1:3-dione into a dimeric keten has not, so far, been observed, and so long as this is the case the substances cannot be regarded as keto-enolic desmotropes.

H. W.

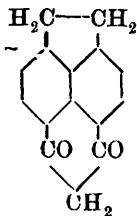
**Malonyl Bromide and a Synthesis of *peri*Acenaphthindandione.** KARL FLEISCHER, HEINRICH HITTEL, and PAUL WOLFF (*Ber.*, 1920, 53, [B], 1847—1852).—The synthesis of a large number of indandiones has been described by Fleischer and his co-workers, but these substances have almost invariably been prepared by the aid of dialkylmalonyl chlorides; attempts to prepare unsubstituted compounds have generally been unsuccessful by reason of the instability of malonyl chloride. Since, however, Fleischer and Wolff (this vol., i, 541) have found that oxalyl bromide is more suitable than oxalyl chloride for ring formation, on account of the greater mobility of the halogen atoms, the authors have turned their attention to the possibilities of malonyl



bromide, and find that this substance also gives considerably better results than the corresponding chloride.

*Malonyl bromide*, pale yellow, heavy liquid with a distinct green fluorescence, which fumes strongly on contact with the atmosphere, and gradually becomes brown when preserved, b. p. 55—57°/11 mm., is prepared by passing an excess of dry hydrogen bromide into ice-cold malonyl chloride. It reacts with acenaphthene dissolved in carbon disulphide in the presence of aluminium chloride to yield *periacenaphthindandione* (annexed formula), yellowish-brown, rectangular rods or small needles united in clusters, which become discoloured, but do not melt, below 300° (a similar experiment with malonyl chloride did not yield this substance). The constitution of the compound is deduced from its oxidation by fuming nitric acid to a mixture of mellophanic acid,  $C_{10}H_6O_8$ , m. p. 239—241°, and naphthalene-1:4:5:8-tetracarboxylic acid, colourless needles, not melting below 300°, which has been obtained previously by Freund and Fleischer (A., 1913, i, 1075) by oxidation of 5-*isobutyryl*acenaphthen-6-carboxylic acid.

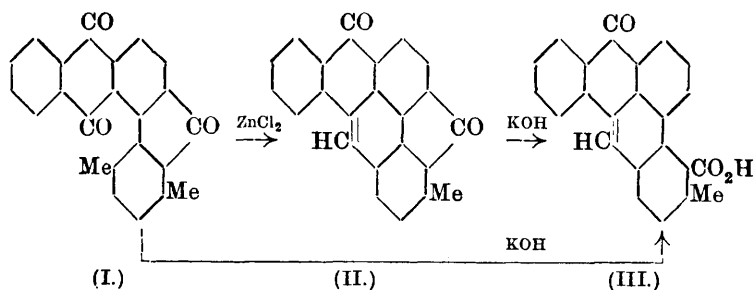
H. W.



### Synthesis of a Phenanthra-anthraquinonefluorenone.

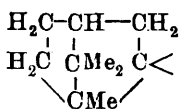
ALFRED SCHAARSCHMIDT and JOHANN HERZENBERG (*Ber.*, 1920, 53, [B], 1807—1814. Compare A., 1919, i, 26).—Chloroanthraquinone-2-carboxylic acid is converted by phosphorus pentachloride into the acid chloride, which condenses with *p*-xylene in the presence of aluminium chloride to yield 1-*chloro*-2-*p*-xyloylanthraquinone,  $C_{14}H_6O_2Cl \cdot CO \cdot C_6H_3Me_2$ , pale yellow, shining needles, m. p. 175—176°, the success of the preparation being greatly dependent on the purity of the xylene. 1-*Amino*-2-*p*-xyloylanthraquinone, compact, reddish-brown needles or leaflets, m. p. 146—147°, prepared by heating the preceding substance with alcoholic ammonia at 180—190°, is diazotised in concentrated sulphuric acid solution, and the product is treated with copper powder, whereby *dimethyl*-1:2-*anthraquinonefluorenone* [3:4-*phthalyl*-5:8-*dimethylfluorenone*] (formula I), yellowish-brown leaflets with an intensely green fluorescence, m. p. 256°, is obtained, together with 1-*methylphenanthra-anthraquinonefluorenone* (formula II), pale brown, amorphous powder, which volatilises without melting at 370—400°, the substances being separable by crystallisation from pyridine or carbon disulphide; minor amounts of 1-*hydroxy*-2-*p*-xyloylanthraquinone (which was not further investigated) and 2-*p*-xyloylanthraquinone, m. p. 159° (which was also prepared from anthraquinone-2-carboxyl chloride, *p*-xylene, and aluminium chloride, and yields an intensely green vat with hyposulphite), were also isolated. The constitution of 1-methylphenanthra-anthraquinonefluorenone follows from its formation by dehydrating agents, such as zinc chloride or sulphuric

acid, from *p*-dimethylantraquino-2:1-fluorenone. Either substance is converted by fusion with potassium hydroxide into a *methylphenanthra-antraquinonecarboxylic acid* (formula III), reddish-brown, amorphous substance, which could not be crystallised by reason of its very sparing solubility in all media; the corresponding *silver* salt was analysed.



H. W.

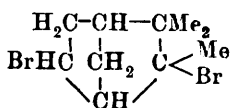
**The Camphene Series. I. Mechanism of the Transformation, *iso*Borneol  $\rightleftharpoons$  Camphene.** HANS MEERWEIN and KONRAD VAN EMSTER (*Ber.*, 1920, 53, [B], 1815—1829).—The unusual phenomena attendant on the conversion of *isoborneol* into camphene have usually been explained by the assumption of the intermediate formation of tricyclene; this hypothesis is, however, rendered improbable by the authors' observation of similar changes in the dehydration of monocyclic alcohols, which are structurally similar to *isoborneol*, and it appears more probable that the intermediate product is a compound with a bivalent carbon atom (annexed formula). Attempts were therefore made to form such a substance, and



camphorhydrazone was, for this purpose, treated with yellow mercuric oxide, thereby giving the mercury compound,  $\text{C}_8\text{H}_{14} \begin{array}{c} < \text{CH}_2 \\ \text{C} \cdot \text{N} \cdot \text{NH} \cdot \text{Hg} \cdot \text{OH} \end{array}$ ,

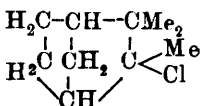
which, when warmed in alcoholic suspension, was, however, smoothly transformed into tricyclene. The idea of the intermediate formation of a compound with bivalent carbon must therefore be abandoned. Tricyclene, which can readily be obtained from easily accessible materials in this manner, has been subjected to an extended examination, and is found to be practically unaltered by protracted treatment with sulphuric acid (33%) at 100° (in similar circumstances, *isoborneol* is almost entirely converted into camphene), and to react with chloroacetic acid with considerably less readiness than does camphene. It is therefore impossible that tricyclene should be an intermediate product of the transformation of *isoborneol* or its esters into camphene. In

general, it is shown that fission of the trimethylene ring in tricyclene occurs most readily between the 1:2- or 1:6-carbon atoms; thus, it is reduced by hydrogen and nickel at 180—200° to *isocamphane*, b. p. 163°, m. p. 57°, possibly after isomerisation to



camphene. Addition of bromine leads to the formation of a liquid *dibromide* (probably annexed formula), from which crystals of pinene or camphene dibromide cannot be caused to separate, and which readily loses one atom of bromine when boiled

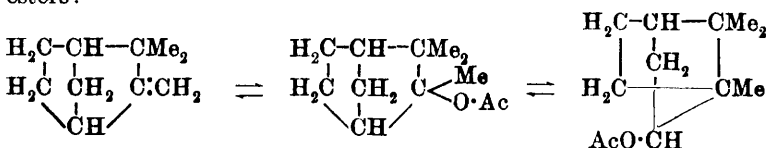
with alcoholic alkali. When gaseous hydrogen chloride is passed into an ethereal solution of tricyclene (or of camphene), crystalline *camphene hydrochloride* (annexed formula), m. p. about 125—127°, separates in 70% yield; the substance is characterised by the unusual mobility



of the chlorine atom and the readiness with which it eliminates hydrogen chloride. The latter phenomenon is rapidly exhibited by the freshly prepared substance, and appears to be

catalytically accelerated by acids. The chloride is slowly decomposed by cold water, with production of camphene hydrate, m. p. 146—147°, and so rapidly by *N/2*-alcoholic alkali that it can be smoothly titrated with such cold solutions. Its most remarkable property, however, is its tendency towards transformation into *isobornyl chloride*, m. p. 158°, which occurs slowly at the ordinary temperature, rapidly in a sealed tube at 130—140°, or by digestion with methyl-alcoholic or ethereal hydrogen chloride at the ordinary temperature. This behaviour explains why previous attempts to prepare camphene hydrochloride have invariably led to products containing more or less *isobornyl chloride*. The latter is far more stable towards *N/2*-alcoholic potassium hydroxide solution, but the chlorine atom can be removed quantitatively by boiling the substance with the reagent for half an hour; pinene hydrochloride is practically unaffected by this treatment. A simple method is thus given for approximately estimating the proportions of camphene hydrochloride, *isobornyl chloride*, and pinene hydrochloride in a mixture of the three products. The camphene hydrochloride-*isobornyl chloride* transformation has been examined in this manner, and it is shown that an equilibrium is attained in the presence of the two chlorides, and also, in all probability, of pinene hydrochloride. Camphene hydrochloride and *isobornyl chloride* therefore behave as desmotropic substances, and this discovery gives the explanation of the transition from the camphor to the camphene series, and vice versa. The formation of *isobornyl esters* from camphene occurs through isomerisation of the camphene hydrate esters primarily formed. The formation of camphene from pinene hydrochloride, *isobornyl chloride*, and other *isobornyl esters*, initially obtained by the action of acidic agents on *isoborneol*, takes place after previous transformation of these

substances into camphene hydrochloride or other camphene hydrate esters:



The change, *isoborneol*  $\rightleftharpoons$  *camphene*, is thus closely analogous to the so-called retro-pinacol transformation (Tiffeneau, A., 1908, i, 117), but the mechanism of the action is not fully elucidated. Most probably it consists of intramolecular atomic displacements, that is, a direct exchange of position between the alkyl radicle and the halogen atom, since it is otherwise difficult to explain the analogous change observed with tertiary alcohols and their esters.

Finally, it has been observed that the camphene obtained from optically active or inactive *isoborneol* is invariably inactive, and the same is generally true for *isoborneol* prepared from camphene. This fact was easily explicable on the assumption that symmetrical tricyclene is intermediately formed, but this hypothesis is no longer tenable. Possibly the desmotropic nature of the *isobornyl* and camphene hydrate esters is in itself sufficient explanation of the observed racemisation, but it appears more probable that, in addition to the main reaction, *isoborneol*  $\rightleftharpoons$  *camphene hydrate*  $\rightleftharpoons$  *camphene*, a subsidiary reversible change, *camphene hydrate*  $\rightleftharpoons$  *tricyclene*, is also involved, in which racemisation occurs. Since this is caused by the presence of acids, it would therefore be expected that transformations of *isoborneol* into camphene, and vice versa, which take place in the absence of acids, would lead to optically active products. This seems actually to be the case, since active *isoborneol* has been prepared by the action of cold formic or acetic acid on camphene in the absence of mineral acid, whilst the possibility of preparing active camphene from *isoborneol* appears to be guaranteed by Ipatiev's conversion of optically active *isoborneol* and *borneol* into active *isocamphane*. H. W.

**Chinese Pine Resin and its Essential Oil.** YRINOSUKE SHINOSAKI and TETSUIJ ONO (*J. Chem. Ind. Tokyo*, 1920, **23**, 45—56).—Pine resin obtained from Wen-Chow, China, contained 8.15% of an essential oil,  $D^{15}_D$  0.8670,  $n^{20}_D$  1.4711,  $[\alpha]_D -31.41^\circ$ , which contained 85% of  $\alpha$ -pinene, a trace of dipentene, and 11% of a tricyclic *sesquiterpene*,  $\text{C}_{15}\text{H}_{24}$ , b. p.  $92-93^\circ/2.5$  mm.,  $D^{15}_D$  0.9408,  $D^{20}_D$  0.9398,  $n^{20}_D$  1.5031,  $[\alpha]_D +47.311^\circ$  in ether, which was isolated as the *monohydrochloride*, needles, m. p.  $58-59^\circ$ , by passing hydrogen chloride into an ethereal solution of the fraction of the essential oil, b. p.  $90-105^\circ/2.5$  mm.

#### CHEMICAL ABSTRACTS.

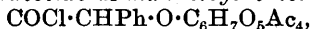
**Glucosides. VII. Constitution of Amygdalin.** P. KARRER, C. NÄGELI, and L. LANG (*Helv. Chim. Acta*, 1920, **3**, 573—583. Compare this vol., i, 370).—The object of the experiments here

described was to ascertain if the still unknown disaccharide of amygdalin is identical with cellobiose. It has been already shown (A., 1919, i, 594; this vol., i, 370, 395) that the silver salts of  $\alpha$ -hydroxy- or  $o$ -hydroxy-carboxylic acids react with acetylbromoglucose, giving the acetylated glucosides and esters of these hydroxy-acids. Tetra-acetylglucosidomandelic acid, obtained in this way from mandelic acid, has now been converted by the action of phosphorus pentachloride into  $\beta$ -tetra-acetyl-*d*-glucosido-*dl*-mandelic acid chloride, which, with the calculated quantity of dry ammonia, gives the corresponding amide. These reactions have been carried out with the inactive mandelic acid residue; the further conversion of the amide into the mandelonitrile glucoside by dehydration and deacetylation has not been proceeded with, as Fischer has shown it to be possible with the active tetra-acetylglucosidomandelic acid amides.

Attempts have been made to apply these methods to the preparation of mandelonitrile celloside. The interaction of inactive silver mandelate and acetobromocellobiose does, indeed, yield hepta-acetylcellosidomandelic acid, but the yield is very small, so that this reaction depends more on the nature of the halogenated compound than on that of the complex silver salt; the smallness of the yield renders it impossible to convert the acid into the corresponding acid chloride and amide. Since, however, hepta-acetylcellosidomandelic acid is not identical with hepta-acetyl-amygdalinic acid, it follows that the non-acetylated acids are not identical, and that the sugar of amygdalin cannot be cellobiose; the  $\beta$ -glucosidic nature of the union of the disaccharide in the two cases is shown by the fact that hydrolysis is effected by emulsin in either case.

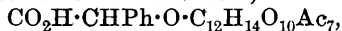
Unsuccessful attempts have been made to induce ethyl mandelate and acetobromocellobiose to react, with formation of ethyl hepta-acetylcellosidomandelate. Hepta-acetylethylcelloside may, however, be obtained from acetobromocellobiose, alcohol, and silver oxide, and, on hydrolysis, yields ethylcelloside, which is the first alkylcelloside known in the crystalline and pure condition (compare Skraup and König, A., 1901, i, 370; 1902, i, 135).

*$\beta$ -Tetra-acetyl-*d*-glucosido-*dl*-mandeloyl chloride,*



forms aggregates of concentric, colourless needles, m. p. 117—119°. The corresponding *amide*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{CHPh} \cdot \text{O} \cdot \text{C}_6\text{H}_7\text{O}_5\text{Ac}_4$ , crystallises in aggregates of colourless, concentric needles, m. p. below 100° after previous sintering.

*Hepta-acetylcellosido-*dl*-mandelic acid,*



forms crystals, m. p. 179—182°,  $[\alpha]_D$  about  $-44^\circ$ , and does not reduce Fehling's solution.

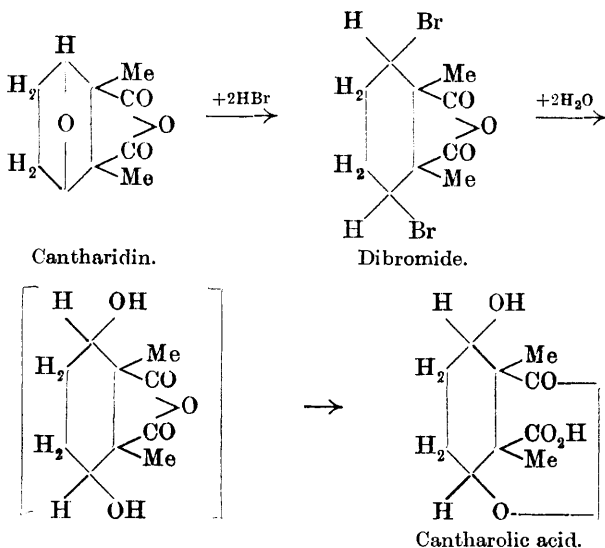
*Hepta-acetylethylcelloside*,  $\text{C}_{12}\text{H}_{14}\text{O}_{10}\text{Ac}_7 \cdot \text{OEt}$ , crystallises in long, white needles, m. p. 184°,  $[\alpha]_D -24.76^\circ$  (in chloroform), and reduces Fehling's solution slightly, possibly owing to slight contamination.

*Ethylcelloside*,  $C_{12}H_{21}O_{10} \cdot OEt$ , is hygroscopic, reduces Fehling's solution in the hot, has  $[\alpha]_D -9.55^\circ$ , and yields the hepta-acetyl derivative on acetylation.  
T. H. P.

**The Influence of the Structure of  $\beta$ -Glucosides on the Action of Emulsin.** EMIL FISCHER (*Zeitsch. physiol. Chem.*, 1919, 176—202).—The action of emulsin on glucosides of glycollic acid,  $\alpha$ -hydroxybutyric acid, mandelic acid, amygdalic acid, cellosidoglycollic acid, their salts, esters, amides, and nitriles, was investigated. The glucosidomandelic acid was prepared from the tetra-acetate of the ethyl ester with baryta, and the glucosido-*d*-mandelic acid was extracted from the glucosides of *d*- and *l*-mandelic acid mixture as the quinine salt. The glucosido-*d*-mandelic acid was also extracted as the cinchonine salt from the amygdalic acid mixture. *Cellosidoglycollic acid* was prepared as follows. Hepta-acetylcellosidoglycollic ester was dissolved with crystalline barium hydroxide in water, and the solution kept for one and a-half to two days at the ordinary temperature. The excess of barium was then removed with sulphuric acid, and the cellosidoglycollic acid precipitated as the lead salt, from which, by treatment with hydrogen sulphide, the free acid,  $C_{14}H_{24}O_{13}$ , decomp.  $195^\circ$ ,  $\alpha_D^{20} -25.12$ — $-25.65^\circ$ , was obtained. The free acids were scarcely affected by small quantities of emulsin. The amides, the esters, and the nitriles were more easily hydrolysed than the other derivatives. The derivatives of glucosido- $\alpha$ -hydroxyisobutyric acid were resistant. The salts and the amide of *d*-mandelic acid, in contradistinction to the *l*-compounds, were not attacked by the enzyme; the methyl ester and nitriles of both, on the other hand, were attacked. A half of the theoretical quantity of dextrose was obtained by the emulsin hydrolysis of *d*-amygdalic acid. The nitrile of cellosidoglycollic acid, unlike the nitrile of glucosidoglycollic acid, was hydrolysed into dextrose and hydrocyanic acid. In general, it may be concluded that glucosides of phenols and phenolcarboxylic acids are degraded with greater ease than glucosides of the aliphatic alcohols and acids of a similar structure.

S. S. Z.

**Cantharidin. IX. Cantharolic Acid.** J. GADAMER (*Arch. Pharm.*, 1920, 258, 171—182. Compare A., 1915, i, 432).—Cantharolic acid is isolated as a by-product from the substances formed by the action of hydrogen bromide in glacial acetic acid solution on cantharidin; it occurs in the portion which is insoluble in ether, together with unchanged cantharidin and cantharic acid, from the latter of which it is separated by taking advantage of its very sparing solubility in boiling alcohol. It is an unsymmetrical, monobasic acid containing a lactone group and a free hydroxyl radicle. Its structure and genetic relationships are indicated by the scheme:



*Cantharolic acid* crystallises in shining rhombs, m. p. 254—256° to 258—260° (decomp.), according to the rate of heating. It is very stable towards alkaline permanganate. It behaves towards alkali as a monobasic acid. The presence of the lactone ring is demonstrated in the usual manner, and fission is found to be more complete than in the case of cantharic acid, but even here the process is complicated by the partial decomposition of the acid by excess of alkali. The hydroxyl group could not be detected by phosphorus trichloride, but the acid is converted by cold concentrated sulphuric acid into the *sulphuric* ester, which was isolated in the form of the *barium* salt,  $C_{10}H_{12}O_8SbA_3 \cdot 3H_2O$ . The free substance was not obtained, since in aqueous solution it somewhat readily undergoes autohydrolysis, with the production of cantharolic acid; the crude material could be resolved into its optical antipodes by brucine in aqueous solution, thus yielding *brucine l-cantharolic acid sulphate*,  $C_{10}H_{14}O_8S \cdot 2C_{23}H_{26}O_4N_2 \cdot 7H_2O$ , very slender needles, and *brucine d-cantharolic acid sulphate*,  $C_{10}H_{14}O_8S \cdot 2C_{23}H_{26}O_4N_2 \cdot 3H_2O$ , coarse, plate-like needles. The brucine salts were converted into the corresponding ammonium salts, and from polarimetric analyses of the latter, the values  $[\alpha]_D - 67.2^\circ$  and  $+67.9^\circ$  are calculated for the free acids in aqueous solution. Hydrolysis of the acids occurs slowly in boiling aqueous solution, but the cantharolic acid produced is almost completely racemised, the effect appearing, however, not to be due to the protracted exposure to a somewhat high temperature. Cantharolic acid is converted by hot concentrated sulphuric acid into cantharic acid.

The resolution of *r*-cantharolic acid has also been attempted by the fractional crystallisation of the brucine salt from water; the

most highly active acid obtained had  $[\alpha]_D - 31.25^\circ$  in aqueous solution, m. p.  $260-263^\circ$  (decomp.). The resolution is remarkable in that the salts only separate when the concentrated solutions are warmed, thus probably indicating the existence of a soluble hydrated and sparingly soluble anhydrous form of the salts, and, further, in that all the fractions yield exclusively levorotatory acids. The explanation of the latter phenomenon is found in the fact that whilst cantharolic acid itself is asymmetric in structure, its hydrate, formed by hydrolysis of the lactone, is symmetrical. In aqueous solution, an equilibrium exists between the lactone and hydrate, which is disturbed by the removal of a portion of the *l*-acid as the brucine salt. A portion of the hydrate therefore passes into the *r*-acid, whilst, simultaneously, inactivation of the dissolved *d*-acid occurs through formation of the hydrate. In this manner, a complete conversion of the *r*-acid into the *l*-acid can be effected through the symmetrical hydrate. In agreement with this explanation, it is found that *l*-cantharolic acid becomes slowly racemised in aqueous solution, and that the same process occurs more rapidly in the presence of an excess of sodium hydroxide. In addition to *r*-cantharolic acid, however, another optically inactive acid is formed in the latter circumstances, and this is produced exclusively when cantharolic acid is heated with alkali hydroxide on the water-bath. This acid is amorphous, and yields an amorphous calcium salt; analyses, taken in conjunction with its mode of formation, indicate that it is 1:2-dimethylcyclohexadienecarboxylic acid, but its physical properties suggest that it is a polymeride of this substance.

H. W.

### Picrotoxin. IX. Degradation of Picrotoxinin by Ozone.

PAUL HORRMANN and HANS PRILLWITZ (*Arch. Pharm.*, 1920, **258**, 200—226).—Further insight into the constitution of picrotoxin (compare A., 1916, i, 566, 827) is afforded by the conversion of picrotoxinin by ozone into formic acid and a ketone,  $\alpha$ -picrotoxininone, which, under the action of dilute sulphuric acid or concentrated hydrochloric acid, suffers a change similar to that of picrotoxin, and yields picrotoxinonic acid. These facts, combined with the behaviour of the substance towards nitric acid, lead the authors to the conclusion that the methylene group in picrotoxin is directly united to a ring carbon atom,  $\text{CH}_2 \cdot \text{C} \begin{array}{l} \diagup \\ \text{R}(\text{C}_{13}\text{H}_{14}\text{O}_6) \end{array} \diagdown$ .

Picrotoxinin is obtained in good yield from picrotoxin by a modification of the method described previously (Meyer and Bruger, A., 1899, i, 226; Horrmann, A., 1912, i, 709), and is converted by ozone in ethyl acetate solution into the corresponding ozonide. Fission of the latter to formic acid and  $\alpha$ -picrotoxininone,  $\text{C}_{14}\text{H}_{14}\text{O}_7$ , is most conveniently effected by violent agitation with cold water. When rapidly crystallised from hot water, the substance separates in shining needles ( $+\text{H}_2\text{O}$ ), and does not exhibit a sharp melting or decomposing point either in the hydrated or anhydrous condition. It has  $[\alpha]_D^{25} - 10.6^\circ$  in



alcoholic solution. It behaves as a dilactone with two free hydroxyl groups. The presence of the ketonic oxygen atom is shown by the isolation of a *semicarbazone*, colourless leaflets ( $+ \text{H}_2\text{O}$ ), which, when air-dried, begins to decompose at  $230^\circ$ , when anhydrous at  $224^\circ$ , but without exhibiting a definite end-point of decomposition, and a *phenylhydrazone*, colourless, silky needles, decomp.  $232\text{--}248^\circ$  after discolouring at  $225^\circ$ . In boiling aqueous solution,  $\alpha$ -picrotoxininone is slowly transformed into  $\beta$ -picrotoxininone,  $\text{C}_{14}\text{H}_{14}\text{O}_7$ , which is more conveniently prepared by heating the  $\alpha$ -derivative under diminished pressure at  $195^\circ$ ; this forms long, anhydrous needles, which are freely soluble in water, and decompose sharply and without melting at  $252\text{--}253^\circ$ . Like the  $\alpha$ -compound, it is a dilactone with two free hydroxyl groups. It has  $[\alpha]_D^{17.5} + 83.023'$  in alcoholic solution, and gives a *semicarbazone*, granular precipitate ( $+ \text{H}_2\text{O}$ ), which commences to decompose at  $222^\circ$ , darkens at  $240^\circ$ , and subsequently passes into a product, which decomposes above  $300^\circ$ , a *phenylhydrazone*, pale yellow precipitate, which decomposes definitely at  $273^\circ$  when rapidly heated, and an *oxime*, cubic crystals, which decomposes sharply at  $255^\circ$ .

$\alpha$ - and  $\beta$ -Picrotoxininone are converted by ice-cold  $N/10$ -aqueous potassium hydroxide solution into two different dicarboxylic acids,  $\text{C}_{14}\text{H}_{18}\text{O}_9$ , which, however, show little tendency to crystallise. The  $\alpha$ -acid is characterised by its *phenylhydrazone*, yellow, amorphous precipitate, which decomposes definitely at  $220^\circ$ ; the  $\beta$ -acid was analysed as the *silver* salt and as the *phenylhydrazone*, pale red needles, which decompose at  $140\text{--}141^\circ$ .  $\alpha$ -Picrotoxininone is transformed by dilute methyl-alcoholic potassium hydroxide solution into amorphous substances and picrotoxinonic acid, needles, which decompose at  $260^\circ$ ,  $[\alpha]_D^{17.5} + 101.046'$  in ethyl alcohol (phenylhydrazine salt of the phenylhydrazone, pale yellow needles, decomp.  $206\text{--}207^\circ$ ), which is identical with the product prepared by Horrmann and Wächter (A., 1916, i, 827) from the ozonide of picrotoxinic acid. The same acid is also obtained by the action of boiling dilute sulphuric acid on  $\alpha$ - or  $\beta$ -picrotoxininone, or from the former by the prolonged action of cold concentrated hydrochloric acid.

Picrotoxinin is converted by cold concentrated hydrochloric acid into two substances, one of which, amounting to about 50% of the material taken, remains undissolved; analyses agree with  $\text{C}_{15}\text{H}_{16}\text{O}_6$ . Two of the oxygen atoms are present in a lactone group, since the substance slowly dissolves in warm potassium hydroxide solution (1 molecule), and the neutral solution yields a *silver* salt,  $\text{C}_{15}\text{H}_{17}\text{O}_7\text{Ag}$ , when treated with silver nitrate. Its other properties, notably its sparing solubility in practically all the usual media, and its high temperature of decomposition (above  $300^\circ$ ), suggest its identity with picrotoxin prepared by Schmidt (A., 1884, 845) by the action of hydrogen chloride on picrotoxin in the presence of ether; attempts to prepare material for comparison by Schmidt's method were not, however, successful. It was not found possible to prepare an acetyl or benzoyl derivative,

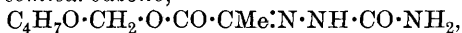
or to estimate the number of hydroxyl groups. The second substance is isolated by extracting the acid solution with ether, or by evaporating it to dryness in a vacuum; the yield is not good, and the substance has not been obtained in the pure state. When dissolved in cold concentrated acetic acid and treated with an excess of phenylhydrazine, it gives a *diphenylhydrazone*,



pale yellow granules, decomp.  $163^\circ$ .

H. W.

**Hydrogenation of Furfuryl Alcohol and Furfuraldehyde to Tetrahydrofurfuryl Alcohol.** HEINRICH WIENHAUS (*Ber.*, 1920, **53**, [B], 1656—1666. Compare Padoa and Ponti, A., 1907, i, 146; Bourguignon, A., 1908, i, 280; Pringsheim and Noth, this vol., i, 249).—Furfuryl alcohol is hydrogenated by Paal's method in aqueous solution and in the presence of sodium hydroxide sufficient to neutralise any liberated hydrogen chloride, or, preferably, in the undiluted condition in the presence of palladised charcoal, with the formation of *tetrahydrofurfuryl alcohol*, colourless liquid, b. p.  $85\text{--}86^\circ/26\text{ mm.}$ ,  $177^\circ/750\text{ mm.}$ ,  $D_{20}^{20} 1.054$ ,  $D_4^{20} 1.0544$ ,  $n_D^{20} 1.44933$ ,  $n_D^{20} 1.45167$ ,  $n_D^{20} 1.45680$ ,  $n_D^{20} 1.46138$ . The corresponding constants of furfuryl alcohol are b. p.  $80^\circ/21\text{ mm.}$ ,  $82\text{--}83^\circ/25\text{ mm.}$ ,  $96^\circ/45\text{ mm.}$ ,  $171^\circ/750\text{ mm.}$ ,  $D_{20}^{20} 1.131$ ,  $D_4^{20} 1.1296$ ,  $n_D^{20} 1.48108$ ,  $n_D^{20} 1.48477$ ,  $n_D^{20} 1.49398$ ,  $n_D^{20} 1.50192$ . The tetrahydroalcohol does not decolorise bromine dissolved in water or light petroleum, is not rapidly oxidised by dilute permanganate solution, and does not colour a pine shaving moistened with concentrated hydrochloric acid. Furfuryl alcohol and its tetrahydro-derivative are markedly hygroscopic. The latter is most readily identified by esterification with pyruvic acid at  $100^\circ$  during two hours, fractionation of the product, and conversion of the crude ester into its *semicarbazone*,



colourless leaflets, m. p.  $184\text{--}186^\circ$ ; a similar method cannot be used with furfuryl alcohol, since the mixture is rapidly transformed, with considerable development of heat, into a dark green, plastic mass. Tetrahydrofurfuryl alcohol gives a *phenylurethane*, small crystals, m. p.  $61^\circ$  (the corresponding compound of furfuryl alcohol crystallises in colourless needles, m. p.  $45^\circ$ ), and a *diphenylurethane*, m. p.  $81^\circ$ .

Hydrogenation of furfuraldehyde in the presence of palladised charcoal and without solvent leads chiefly to the formation of tetrahydrofurfuryl alcohol.

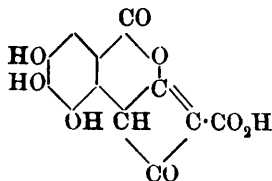
H. W.

**Galloflavin.** J. HERZIG (*Annalen*, 1920, **421**, 247—282).—Tetramethylgalloflavin readily loses one methoxy-group under the influence of alkali hydroxides, and passes into trimethylisogalloflavin, which has been shown to contain a carboxyl group and a lactone ring. It has now been found possible to degrade the substance by a series of comparatively simple reactions to 3:4:5-

trimethoxyphthalide,  $C_6H(OMe)_3 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix} O$  (compare Bargellini

and Molina, A., 1912, i, 773), and thus to prove the presence of the group

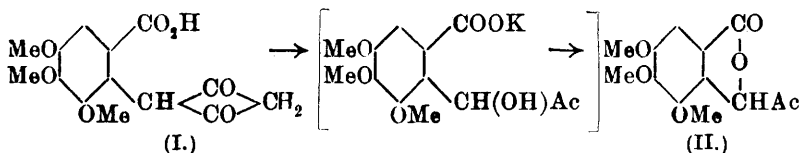
$C_6H(OH)_3 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix} O$  in *isogalloflavin*.



After making allowance for the known presence of the carboxyl group, the residue,  $C_3HO$ , remains, which is accounted for by the existence of another ring, thus

leading to the annexed formula for *isogalloflavin*.

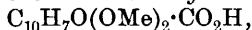
[With ELISABETH EYWELING and HEDWIG BRUNNER].—Trimethyl*isogalloflavin* decomposes when distilled into carbon dioxide, and a substance,  $C_{11}H_3O_3(OMe)_3$ , which does not react with diazomethane or acetylating agents, and in which the lactone ring is only shown to be present with difficulty; under definite conditions of successive treatment with methyl-alcoholic aqueous potassium hydroxide solution and acid, it is possible to convert it into the substance (I), m. p. 74–77°; the latter is converted by the further action of alkali hydroxide and potassium formate into a product (II), m. p. 134–136°, and this substance is further transformed by alkali into 3:4:5-trimethoxyphthalide and potassium acetate.



The possibility of using the tetramethyl*isogalloflavincarboxylic* acid, m. p. 132–135° (compare A., 1910, i, 676), as initial material for the study of the degradation of *isogalloflavin* has been investigated, but its method of preparation is too cumbersome for this purpose; its *methyl* ester has m. p. 53–55°.

The action of zinc dust and aqueous potassium hydroxide solution on *isogalloflavin* leads to the formation of the two acids,  $C_{12}H_{10}O_7$  and  $C_{10}H_8O_5$ .

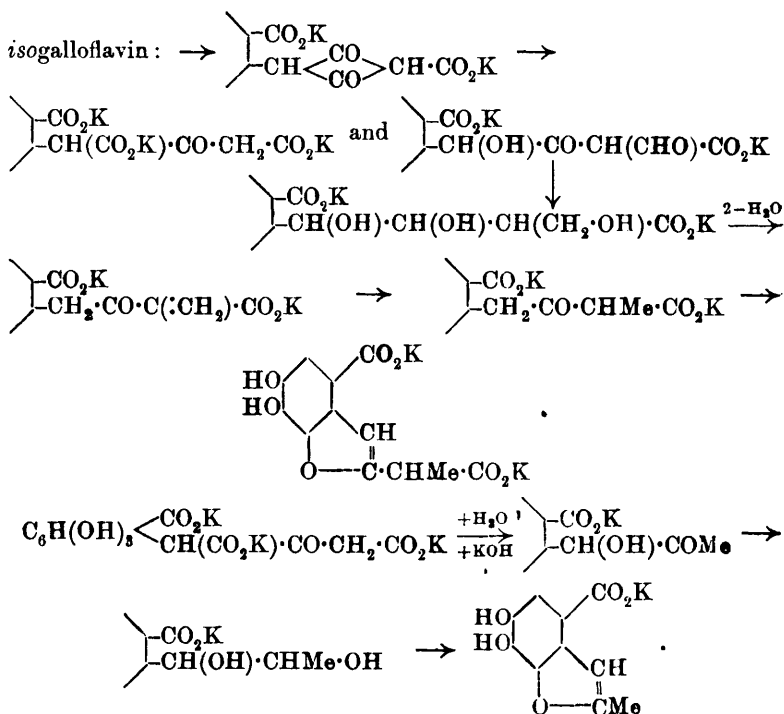
[With FRANZ SCHAFFER].—The dihydroxy-dicarboxylic acid,  $C_{12}H_{10}O_7$ , silvery leaflets, m. p. 191–194° (decomp.), which is readily oxidised in aqueous solution, is characterised by its conversion by diazomethane into a *tetramethyl* derivative, m. p. 101–103°, which is hydrolysed to the corresponding *dimethoxy-dicarboxylic acid*, m. p. 200–203°; the latter is in part unchanged by distillation under greatly reduced pressure, and in part transformed into the *monocarboxylic acid*,



m. p. 132–135° (*methyl* ester, oil). The dicarboxylic acid is unaffected by acetic anhydride, sodium acetate, and zinc dust. The acid, m. p. 191–194°, is converted by methyl-alcoholic hydrogen chloride into the *methyl* ester,  $C_{10}H_6O(OH)_2(CO_2Me)_2$ , m. p.

153—156°, which yields the corresponding *diacetyl* derivative, m. p. 71—73°. The dimethoxydicarboxylic acid is unaffected by zinc and potassium hydroxide solution, by the latter alone under pressure, and at elevated temperature by treatment with sulphuric acid, or by oxidation with chromic acid.

[With LUDMILLA PARNAS.]—The acid,  $C_{10}H_8O_5$ , could not be isolated in the pure condition by reason of its very ready oxidisability in solution; the following series of derivatives, however, proves it to be a dihydroxymonocarboxylic acid. *Trimethyl* compound (from the acid and methyl sulphate in the presence of sodium hydroxide), colourless platelets, m. p. 101—103°, which is hydrolysed to the corresponding *acid*,  $C_9H_5O(OMe)_2 \cdot CO_2H$ , m. p. 185—188°, which distils unchanged under diminished pressure; *methyl ester*,  $C_9H_5O(OH)_2 \cdot CO_2Me$  (from the crude acid and methyl-alcoholic hydrogen chloride), which is very difficult to purify, has m. p. 184—190°, and yields a *diacetyl* derivative, m. p. 109—112°. The production of these acids is represented by the schemes:

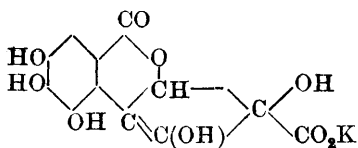


The action of zinc dust and potassium hydroxide on galloflavin proceeds in the same manner, but the yields of the reaction products are much smaller. Attempts to convert the acid  $C_{12}H_{10}O_7$  into  $C_{10}H_8O_5$  by prolonging the action of zinc and

potassium hydroxide on *isogalloflavin* or on the dihydroxydicarboxylic acid did not lead to the desired result.

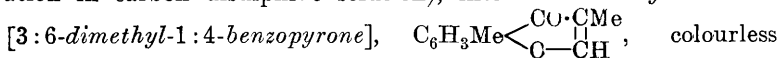
[With KARL TRENKLE, MARIANNE SCHLEIFFER, and ELISABETH EYWELING.]—The action of acetic anhydride, sodium acetate, and zinc dust on *isogalloflavin* and its derivatives follows a somewhat complicated course. In these circumstances, *isogalloflavin* itself (which has been shown previously to give a normal triacetyl derivative with acetic anhydride and sodium acetate) yields a *tetraacetyl* compound, m. p. 203—206° (decomp.) after becoming discoloured from about 180°, and the same substance can also be prepared from triacetyl*isogalloflavin* in similar circumstances. Similarly, trimethyl*isogalloflavin* yields *acetyltrimethylisogalloflavin*, long, colourless needles, m. p. 138—140°. On the other hand, the methyl esters of trimethyl- and triacetyl-*isogalloflavin* are unchanged by this treatment, for which the presence of a free carboxyl group appears essential. The exact mechanism of the reaction has not been fully elucidated. Carbon dioxide is certainly eliminated during the process, and it appears probable that the acetyl group takes the place of the carboxyl group; on the other hand, since the action only occurs in the presence of zinc dust (acetic anhydride and zinc acetate do not even cause acetylation of the free hydroxyl groups of *isogalloflavin*), it is possible that the carbonyl group adjacent to the carboxyl radicle is reduced, and the secondary alcoholic group is then acetylated. Attempts to gain further insight into the action by a study of analogous substances do not afford much general information. Thus, 3:4:5-trimethoxyphthalidecarboxylic acid gave an almost quantitative yield of the corresponding phthalide, both in the presence and absence of zinc dust, whilst benzilic acid yielded small quantities of  $\beta\beta$ -diphenylpropionic acid. With 5:6-dimethoxyphthalidecarboxylic acid, a more complex change occurs, which does not give rise to the formation of the phthalide.

The presence of a carboxyl group in *isogalloflavin* is clearly demonstrated by its direct conversion into the methyl ester, m. p. 300—305° after previous darkening by methyl-alcoholic hydrogen chloride. In similar circumstances, galloflavin is absolutely unaffected. The conversion of galloflavin into *isogalloflavin* appears to be due to a change of the type of the benzilic acid transformation brought about in the five-membered ring of the former by potassium hydroxide, yielding the intermediate product (annexed formula), which passes, by loss of water, into *isogalloflavin*. H. W.

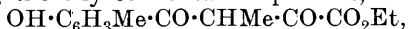


**Ring Formation.** KARL VON AUWERS (*Annalen*, 1920, **421**, 1—118).—[With ELISABETH LÄMMERHIRT.]—In view of the unexpected formation of 3:6-dimethyl-2:3-dihydro-1:4-benzopyrone, m. p. 34—35° (semicarbazone, m. p. 232°), by the action of diethyl-

aniline on *m*- $\alpha$ -bromoisobutyryl-*p*-cresol (A., 1917, i, 277), the constitution of the product has been rigidly proved, not only synthetically (*loc. cit.*), but also by its conversion through the 3-bromo-derivative, crystals, m. p. 70—71° (obtained by bromination in carbon disulphide solution), into 3:6-dimethylchromone



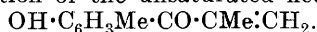
needles, m. p. 61—62°, b. p. 299—301°/atm., or 165—168°/15 mm., by means of boiling dimethylaniline. 3:6-Dimethyl-1:4-benzopyrone, which yields *m*-propionyl-*p*-cresol and formic acid by boiling with alcoholic sodium ethoxide, has also been prepared by condensing *m*-propionyl-*p*-cresol and ethyl oxalate by means of sodium, heating the oily condensation product,



with concentrated hydrochloric acid, and eliminating carbon dioxide from the resulting 3:6-dimethyl-1:4-benzopyrone-2-carboxylic acid.

Contrary to the statement of Auwers and Krollpfeiffer (A., 1915, i, 442), 3-bromo-6-methyl-2:3-dihydro-1:4-benzopyrone is converted into 6-methyl-1:4-benzopyrone by boiling with dimethylaniline.

The conversion of *m*- $\alpha$ -bromoisobutyryl-*p*-cresol into 3:6-dimethyl-2:3-dihydro-1:4-benzopyrone (see above) must involve the intermediate formation of the unsaturated ketone,



In order to ascertain whether the conversion of such unsaturated ketones into benzopyrones is a general reaction, the condensation of *p*-tolyl methyl ether and crotonyl chloride by means of aluminium chloride has been examined. The reaction is complicated, and one or more of five different products may be obtained, according to the experimental conditions. It has been established, however, that if the ethereal solution of the initial condensation product is repeatedly shaken with aqueous sodium hydroxide, three products are obtained: (1) the methyl ether of *m*-crotonyl-*p*-cresol,  $\text{OMe} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO} \cdot \text{CH} : \text{CHMe}$  (only isolated as the disemicarbazide derivative,

$\text{OMe} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{C}[\text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2] \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , m. p. 205—206°), (2) 2:6-dimethyl-2:3-dihydro-1:4-benzopyrone, m. p. 54—55° (semicarbazone, m. p. 203°), and (3) 7-hydroxy-3:4-dimethylhydrindone, whilst if the ethereal solution is directly distilled under diminished pressure, the chief product is *m*-crotonyl-*p*-cresol,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO} \cdot \text{CH} : \text{CHMe}$ , yellow solid, m. p. 65—66°, which is quantitatively converted into the isomeric 2:6-dimethyl-2:3-dihydro-1:4-benzopyrone by distillation at the ordinary pressure (b. p. 277—278°), or by treatment with aqueous sodium hydroxide.

2:6-Dimethyl-2:3-dihydro-1:4-benzopyrone has been synthesised by condensing  $\beta$ -chlorobutyryl chloride, b. p. 51—53°/21 mm., with *p*-tolyl methyl ether, and eliminating hydrogen chloride from the resulting *m*- $\beta$ -chlorobutyryl-*p*-cresol by means of sodium

carbonate. By bromination, it yields 3-bromo-2:6-dimethyl-2:3-dihydro-1:4-benzopyrone, m. p. 104—105°, which is converted into 2:6-dimethyl-1:4-benzopyrone, m. p. 102—103°, by boiling with dimethylaniline; the benzopyrone has also been prepared by condensing the methyl ether of *m*-acetyl-*p*-cresol with ethyl acetate and boiling the product,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COMe}$ , with hydriodic acid.

There is little doubt that the inability of *m*- $\alpha$ -bromoisobutyryl-*p*-cresol to give a trimethylcoumaranone is due to the *gem*-dimethyl group. That this group does not hinder the formation of a 6-ring is shown by the following experiments with *p*-hydroxy-*m*-tolylisobutenyl ketone. The reaction in carbon disulphide between equal molecular quantities of *p*-tolyl methyl ether and  $\beta\beta$ -dimethylacrylyl chloride in the presence of aluminium chloride yields different products, according to the conditions. 7-Hydroxy-3:3:4-

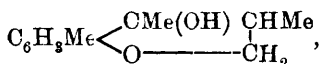
trimethylhydrindone,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Me}\langle\text{CMe}_2\text{CO}\rangle\text{CH}_2$ , colourless prisms, m. p. 67—68° (sodium derivative; semicarbazone, needles, m. p. 201—202°), is obtained in small quantity. When an ethereal solution of the reaction product is shaken with sodium hydroxide solution and the resulting oil is treated with semicarbazide, the semicarbazone, m. p. 199—200°, of 2:2:6-trimethyl-2:3-dihydro-1:4-benzopyrone and *m*- $\beta$ -semicarbazidoisovaleryl-*p*-cresol,

$\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 148—149° (to be described elsewhere), are obtained. When the reaction product is not treated with sodium hydroxide, the principal product is *p*-hydroxy-*m*-tolyl isobutenyl ketone,

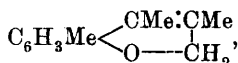
$\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}_2$ , sulphur-yellow prisms and needles, m. p. 50—50.5°, b. p. 159—160°/15 mm.,  $D_4^{25}$  1.0376,  $n_D$  1.56280,  $n_D$  1.57187 at 53.8°. This ketone is converted into 2:2:6-trimethyl-2:3-dihydro-1:4-benzopyrone by heating at 277—278°, by boiling with diethylaniline (but not with pyridine), by treatment with dilute sodium hydroxide solution or with sodium methoxide solution, or with boiling absolute alcohol containing a few drops of concentrated hydrochloric (but not dilute sulphuric acid at the ordinary temperature) acid. It is reduced in methyl-alcoholic solution by hydrogen and colloidal palladium to *p*-hydroxy-*m*-tolyl isobutyl ketone (semicarbazone, m. p. 204°), reacts additively with hydrogen chloride in cold glacial acetic acid to form *p*-hydroxy-*m*-tolyl  $\beta$ -chloroisobutyl ketone,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CMe}_2\text{Cl}$ , prisms, m. p. 53—55° (which is smoothly converted into 2:2:6-trimethyl-2:3-dihydro-1:4-benzopyrone by sodium hydroxide solution), and by bromination in cold carbon disulphide solution yields the dibromide,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CMe}_2\text{Br}$ , faintly yellow needles, m. p. 70—71°; this is converted by dilute sodium hydroxide solution into 3-bromo-2:2:6-trimethyl-2:3-dihydro-1:4-benzopyrone, m. p. 75—76°, which is also obtained by the careful bromination of the trimethylchromanone.

The section closes with a comparison of the physical properties

of 6-methyl-, 3:6- and 2:6-dimethyl-, and 2:2:6-trimethyl-2:3-dihydro-1:4-benzopyrones, and of the ease of formation of their semicarbazones, oximes, *p*-nitrophenylhydrazones, 3-bromo- and 3:3-dibromo-derivatives; the conversion of the bromo-derivatives into benzopyrones, of the dihydrobenzopyrones into dihydrobenzopyranols by Grignard reagents, and of the last into benzopyrens, is also described. Curiously enough, 2:2:6-trimethyldihydrobenzopyrone and magnesium methyl iodide in ethereal solution give visible signs of interaction, but, on working up the product, the unchanged trimethyldihydrobenzopyrone is obtained. 3:4:6-Trimethyl-2:3-dihydro-1:4-benzopyranol,



stout prisms, m. p. 123—124°, is converted by phosphoric oxide on the water-bath into 3:4:6-trimethyl- $\Delta^3$ -benzopyren,



b. p. 135—136°/13 mm. 2:4:6-Trimethyldihydrobenzopyran-4-ol, prisms, m. p. 89—90·5°, and 2:4:6-trimethyl- $\Delta^3$ -benzopyren, b. p. 138·5—139·5°/25 mm., have been prepared.

[With H. SCHÜTTE.]—Since the facility of formation of coumaranones is increased by meta-substituents in the phenolic portion of the molecule (Auwers and Pohl, A., 1914, i, 981), 3:5-dimethylcoumaran-2-one, for example, being the most easily formed and the stablest of the coumaranones, it becomes of interest to ascertain whether the meta-substituting methyl groups or the *gem*-dimethyl group in 6- $\alpha$ -bromoisobutyryl-*m*-5-xylenol exercises the predominating influence when this compound is treated with reagents for the removal of hydrogen bromide; in the latter case, a tertiary alcohol would be expected, in the former a coumaranone or a dihydrobenzopyrone. The only product obtained when equal molecular quantities of *m*-5-xylyl methyl ether and  $\alpha$ -bromoisobutyryl bromide are heated with aluminium chloride in carbon disulphide solution is 1:1:3:5-tetramethylcoumaran-2-one, colourless needles, m. p. 41—42°, b. p. 130°/12 mm.,  $D_4^{18.2}$  1·0620,  $D_4^{20}$  1·060,  $n_D$  1·53765,  $n_D$  1·54359,  $n_B$  1·56110,  $n_F$  1·57820 at 18·2°, which has also been prepared by methylating 1:3:5-trimethylcoumaranone with sodamide and methyl iodide in dry ethereal solution. The compound does not react with semicarbazide or *p*-nitrophenylhydrazine, and is only slowly attacked by bromine in carbon disulphide, yielding 4-bromo-1:1:3:5-tetramethylcoumaranone, silky needles, m. p. 74·5°, which has also been prepared by the interaction of 2-bromo-*m*-5-xylyl methyl ether, m. p. 24—25°, b. p. 137—139°/20 mm. (obtained by methylating the corresponding xylenol with methyl sulphate), and  $\alpha$ -bromoisobutyryl bromide in the presence of aluminium chloride. 4:6-Dibromo-1:1:3:5-tetramethylcoumaranone, colourless needles, m. p. 151—152°, is

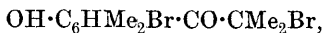


obtained by warming 1:1:3:5-tetramethylcoumaranone with bromine in glacial acetic acid solution, or by treating it with bromine and 2% of aluminium.

The reaction between *m*-5-xylyl methyl ether, isobutyryl chloride, and aluminium chloride in carbon disulphide leads to the formation of 5-hydroxy-*m*-6-xylyl isopropyl ketone,



stout prisms, *m. p.* 93—94°, *b. p.* 160—165°/24 mm., which does not form an oxime or a semicarbazone, but yields a *p*-nitrophenylhydrazone, yellow leaflets, *m. p.* 181—182°, and is converted by bromine in glacial acetic acid, according to the conditions, into 2-bromo-5-hydroxy-*m*-6-xylyl  $\beta$ -bromoisopropyl ketone,

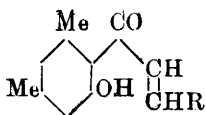


stout prisms, *m. p.* 128—129°, or 2:4-dibromo-5-hydroxy-*m*-6-xylyl  $\beta$ -bromoisopropyl ketone, stout needles, *m. p.* 154°, each of which is smoothly converted into the corresponding brominated coumaranone by aqueous sodium hydroxide or boiling diethylaniline.

*m*-5-Xylyl methyl ether, butyryl chloride, and aluminium chloride react in carbon disulphide solution to give 5-hydroxy-*m*-6-xylyl propyl ketone,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{COPr}^i$ , stout prisms, *m. p.* 58—59°, and its methyl ether, *b. p.* 162°/16 mm., the latter being obtained even when an excess of aluminium chloride is used. The hydroxy-ketone does not react with hydroxylamine or semicarbazide, but forms a *p*-nitrophenylhydrazone, yellow crystals, *m. p.* 162—162.5°. The acetate, *b. p.* 173—175°/12 mm., by treatment with bromine (1 mol.) in carbon disulphide, yields 5-acetoxy-*m*-6-xylyl  $\alpha$ -bromopropyl ketone,  $\text{OAc}\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{CO}\cdot\text{CHBrEt}$ , *m. p.* 36.5—38.5°, which is converted by hot aqueous-alcoholic sodium hydroxide into 3:5-dimethyl-1-ethylcoumaranone (see following section). When 5-hydroxy-*m*-6-xylyl propyl ketone is brominated in the same way as its acetate, the product is 2-bromo-5-hydroxy-*m*-6-xylyl propyl ketone, leaflets, *m. p.* 108—109°, but when two and three molecules of bromine are used, the product is 2-bromo-5-hydroxy-*m*-6-xylyl  $\alpha$ -bromopropyl ketone, *m. p.* 112.5—113.5°, and 2:4-dibromo-5-hydroxy-*m*-6-xylyl  $\alpha$ -bromopropyl ketone, colourless needles, *m. p.* 124—125°, respectively. 2-Bromo-5-hydroxy-*m*-6-xylyl propyl ketone has also been prepared from 2-bromo-*m*-5-xylyl methyl ether, butyryl chloride, and aluminium chloride, a remarkable by-product of the reaction being 2:4-dibromo-*m*-5-xylyl methyl ether, *m. p.* 108—109° (also prepared by methylating the dibromoxylene).

4-Bromo-3:5-dimethyl-1-ethylcoumaranone, flattened prisms, *m. p.* 60—61°, is smoothly obtained by treating an acetone solution of 2-bromo-5-hydroxy-*m*-6-xylyl  $\alpha$ -bromopropyl ketone with aqueous sodium hydroxide; by bromination in carbon disulphide, it yields 1:4-dibromo-3:5-dimethyl-1-ethylcoumaranone, *m. p.* 44—45°.

[With R. DÖLL.]—The object of this section is to ascertain



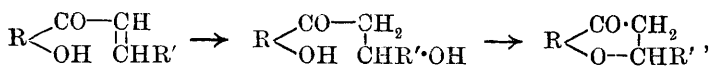
whether unsaturated hydroxy-ketones of the annexed type yield coumaranones or dihydrobenzopyrones by treatment with ring-forming agents.

The reaction between *m*-5-xylyl methyl ether, crotonyl chloride, and aluminium chloride in carbon disulphide leads to the formation of 2:5:7-trimethyl-2:3-dihydrobenzopyrone,  $C_6H_2Me_2 \begin{matrix} \text{CO} \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} - \text{CH} \text{Me} \end{matrix}$ , silky, needles, m. p. 66—67°, b. p. 172—174°/23 mm. (*semicarbazone*, m. p. 219—220° [decomp.]; *p*-nitrophenylhydrazone, orange-red needles, m. p. 230—231°); no trace of a coumaranone could be discovered, although thorough search was made. 3:5-Dimethyl-1-ethylcoumaranone, b. p. 152—154°/18 mm.,  $D_4^{20}$  1.0667,  $n_D$  1.53689,  $n_D$  1.54240,  $n_B$  1.55907,  $n_T$  1.57403 at 20.5°, is prepared by treating *m*-5-xylyl methyl ether and  $\alpha$ -bromobutyryl bromide with aluminium chloride in carbon disulphide solution, and shaking the resulting bromobutyroxyleneol with aqueous methyl-alcoholic potassium hydroxide; the coumaranone must be purified through its acetate,  $C_6H_2Me_2 \begin{matrix} \text{C(OAc)} \\ \diagdown \quad \diagup \\ \text{O} \end{matrix} \text{CEt}$ , b. p. 175—179°/23 mm., obtained by digesting it with acetyl chloride. The coumaranone does not react with semicarbazide under the usual conditions, and is converted by *p*-nitrophenylhydrazine into the *pp'*-dinitro-osazone of 5-hydroxy-*m*-6-xylyl ethyl diketone,  $OH \cdot C_6H_2Me_2 \cdot C(N \cdot NH \cdot C_6H_4 \cdot NO_2) \cdot CEt \cdot N \cdot NH \cdot C_6H_4 \cdot NO_2$ , orange-red crystals, m. p. 246°.

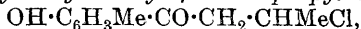
Under the influence of aluminium chloride, *m*-5-xylyl methyl ether and  $\beta\beta$ -dimethylacrylyl chloride in carbon disulphide yield 2:2:5:7-tetramethyl-2:3-dihydro-1:4-benzopyrone, stout prisms, m. p. 71—72°, b. p. 163—166°/17 mm. (*semicarbazone*, needles, m. p. 198—199°; *p*-nitrophenylhydrazone, stout, brick-red prisms, m. p. 210—211°); absence of 3:5-dimethyl-1-isopropylcoumaranone among the by-products was not definitely ascertained. This coumaranone, b. p. 156°/20 mm.,  $D_4^{20}$  1.0472,  $n_D$  1.53396,  $n_D$  1.53955,  $n_B$  1.55610,  $n_T$  1.57256 at 21.0°, was prepared from *m*-5-xylyl methyl ether and  $\alpha$ -bromoisovaleryl bromide in the usual way.

By warming an alcoholic solution of benzaldehyde and 4-hydroxy-*m*-tolyl methyl ketone with 50% sodium hydroxide at 50° for many hours, and acidifying the resulting sodium salt, 4-hydroxy-*m*-tolyl styryl ketone,  $OH \cdot C_6H_3Me \cdot CO \cdot CH : CHPh$ , stout, orange, apparently rhombic crystals, m. p. 111°, is obtained, which evidently is not convertible into a bicyclic compound by alkali; by variations from the conditions of preparation mentioned above, however, 6-methylflavone is formed in place of, or together with, the ketone. The ketone forms a dibromide, pale yellow, hexagonal prisms, m. p. 151—152°, which in warm alcoholic solution is easily converted into 3-bromo-6-methylflavanone, colourless leaflets, m. p. 130°, by *N*/10-sodium hydroxide.

The conversion of an *o*-hydroxy-ketone with an unsaturated side-chain into a bicyclic compound by alkali may be represented by the scheme:



the intermediate compound being unstable in the presence of alkali. An unsuccessful attempt to prepare such a compound has been made. *4-Hydroxy-m-tolyl β-chloropropyl ketone*,



colourless needles, m. p. 66—67°, prepared from the unsaturated ketone and hydrogen chloride in glacial acetic acid at 0°, forms an *acetate*, prisms, m. p. 86—87° (which is best prepared, however, by heating the unsaturated ketone with acetyl chloride at 100° in a sealed tube), in which, however, all attempts to replace the chlorine atom by an acetoxy-group failed.

The paper closes with a review of the most important results recorded in the three preceding sections and in thirteen papers published during the last six years in connexion with the formation of coumaranones, dihydrobenzopyrones, and hydroxyhydrindones.

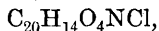
C. S.

### The Chelidonium Alkaloids. II. [Quantitative Estimation of the Methylenedioxy-group in Alkaloids.]

J. GADAMER (*Arch. Pharm.*, 1920, **258**, 148—167. Compare this vol., i, 75).—The first part of the communication is devoted to a full description of the experimental evidence on which the author bases his formula for *allocryptopine*, a preliminary announcement of which has been made previously (*loc. cit.*). *allocryptopine* is converted by phosphoryl chloride into *isoallocryptopine* chloride, colourless needles, m. p. 200—202°, which immediately develop a dark violet coloration with concentrated sulphuric acid, and this is identical in all respects (the mixture has m. p. 199—202°) with the product obtained by the action of potassium chloride on dihydroberberine methosulphate; further, *isoallocryptopine* chloride is transformed by silver methyl sulphate into a product, m. p. 195—198°, which is identical with dihydroberberine methosulphate, m. p. 197—200° (Perkin, T., 1916, **109**, 834). Again, *allocryptopine* is reduced by sodium amalgam in sulphuric acid solution to dihydro*allocryptopine*, m. p. 167—168°, which is converted by phosphoryl chloride into *isodihydroallocryptopine* chloride, m. p. 248—250° (decomp.), which is identical with tetrahydroberberine methochloride, m. p. 249—251° (decomp.), and the identity of the compounds is confirmed by comparison of their bromides.

When the O-acetyl derivative of chelidonine is oxidised with mercuric acetate, a colourless, non-basic substance is obtained, which, particularly in acid solution, gradually acquires an intensely reddish-yellow coloration and basic properties. Its behaviour is thus strikingly analogous to that of dihydrochelerythrine described

by Karrer (A., 1917, i, 349). Chelerythrine itself can, however, scarcely be directly related to chelidonine, but appears to be closely allied to  $\alpha$ -homochelidonine. A preliminary examination of the subject reveals the following facts. Chelerythrine contains two methoxy- and one methylenedioxy-groups. A keto-group cannot, therefore, be present, and the reactions considered by Karrer to be due to the carbonyl group are to be regarded as occurring in the same manner as with cotarnine and berberine. Karrer's assumption of the elimination of a chain,  $C_5H_5O$ , in the formation of chelalbin compounds is highly improbable, and in this connexion it is to be noted that berberine yields additive compounds with Grignard's reagents. In its salts, chelerythrine is a quaternary base, the properties of which are due to the nitrogen atom (and not to basic oxygen, as postulated by Karrer). The free ammonium base appears incapable of existence; when the salts are treated with alkali, it immediately passes into the colourless carbinol base. It is extremely probable that an analogue of chelerythrine exists in nature which forms a chloride,



differing from sanguinarine chloride,  $C_{20}H_{16}O_4NCl$ , by containing two less hydrogen atoms, and it appears to have been occasionally mistaken for the latter. The substance ultimately obtained from O-acetylhomochelidonine has m. p. 160—162°, and is identical with dihydrochelerythrine obtained by Karrer's method from an authentic specimen of chelerythrine (Karrer gives m. p. 143—144°, but his product is shown to be contaminated with impurities present in Merck's preparation from *Sanguinaria canadensis*). The identity of the products is further established by the fact that the material from either source becomes oxidised on exposure to air to chelerythrine, which is identified as the cyanide, m. p. 258° (for which Karrer gives varying melting points).

[With WINTERFELD.]—Under the action of concentrated sulphuric acid, substances containing the methylenedioxy-group readily lose formaldehyde, which is capable of further condensation; its action on phloroglucinol has been adapted by Weber and Tollens to the qualitative detection and quantitative estimation of the methylenedioxy-group, and the reaction has been occasionally applied to alkaloids (see, for example, Gaebel, A., 1910, i, 502), with which, however, it does not give very definite results. The method has been investigated further, and the following process is recommended. Pure phloroglucinol (0.3 gram) is dissolved in a warm mixture of water (15 c.c.) and concentrated sulphuric acid (15 c.c.), and the weighed quantity of alkaloid dissolved in water (5 c.c.) is added. The mixture is shaken until a clear solution is obtained, and treated with concentrated sulphuric acid (10 c.c.). The flask is closed with a funnel and heated over wire gauze until the solution boils gently and a precipitate begins to form. It is then warmed in the water-bath at 70—80° for three hours. After twenty-four hours, the precipitate is filtered

through a Gooch crucible, washed with water (60 c.c.), dried at  $100^{\circ}$  for four hours, and weighed. The weight of phloroglucide divided by 9.857 gives the amount of methylene,  $\text{CH}_2$ . The method has several sources of error, and should therefore be effected with differing amounts of alkaloid and occasional blank experiments. The results are to be regarded as minimal values. The markedly low values are due to the fact that the eliminated formaldehyde only combines in part with the phloroglucinol to yield an insoluble phloroglucide, whilst another portion combines with the alkaloid or with alkaloid and phloroglucinol. The basic substances naturally remain dissolved in the acid, but may be partly precipitated when the latter is diluted with water (the precipitate should therefore be thoroughly drained before washing is commenced). The frequent observation during the examination of the colour reactions of alkaloids with concentrated sulphuric acid, that the mixture becomes turbid on exposure to moisture (for example, with bulbocapnine), thus receives its explanation. In general, the method is sufficiently accurate to allow a decision as to whether one or two methylenedioxy-groups are present. Two such groups are thus shown to be contained in chelidonine, corycavine and corycavamine, and one in corycavidine. H. W.

**Chelerythrine.** K. HUGO BAUER and K. TH. HEDINGER (*Arch. Pharm.*, 1920, **258**, 167—170).—For the preparation of the alkaloid [colourless, prismatic leaflets from alcohol (+ EtOH), m. p.  $207^{\circ}$ ], the total alkaloids from the *Sanguinaria* root are mixed with milk of lime, the product is dried, and extracted with a mixture of equal parts of ether and benzene. The alkaloids are removed from the extract with citric acid, and subsequently precipitated with ammonia, and again dissolved in benzene. The residue obtained after removal of the latter is repeatedly crystallised from ethyl alcohol. The following salts have been prepared: hydrochloride,  $\text{C}_{21}\text{H}_{17}\text{O}_4\text{N}\cdot\text{HCl}\cdot\text{H}_2\text{O}$ , egg-yellow needles (compare Schmidt, König, and Tietz, A., 1893, i, 496; Fischer, A., 1901, i, 742; Karrer, A., 1917, i, 349); *hydriodide*, anhydrous, dark red needles, which become pale brown at  $150$ — $160^{\circ}$ ; tartrate, anhydrous, dark red crystals arranged in rosettes; *oxalate*, reddish-yellow needles; *methyl sulphate*,  $\text{C}_{21}\text{H}_{17}\text{O}_4\text{N}\cdot 2\text{Me}_2\text{SO}_4\cdot 3\text{MeOH}$ , short, golden-yellow needles. Contrary to the observation of Tietz, chelerythrine hydriodide or hydrochloride does not evolve methyl iodide when treated with hydriodic acid at a temperature below  $125^{\circ}$ , and hence the alkaloid does not contain a methoxy-group. On the other hand, evolution of methyl iodide is observed at  $145^{\circ}$  and again at  $275^{\circ}$  in the estimation of the methylimino-groups in the hydriodide (at  $165^{\circ}$  and  $245^{\circ}$ , respectively, with the hydrochloride), thus indicating the presence of the  $\text{NMe}_2$  group.

Chelerythrine absorbs two atoms of hydrogen when catalytically hydrogenated in the presence of colloidal palladium, but the product has not yet been obtained in the pure state.

H. W.

**Oxidation of Quinine with Hydrogen Peroxide.**

MAXIMILLIAN NIERENSTEIN (*Biochem. J.*, 1920, **14**, 572—573).—An examination of the oxidation products resulted only in the isolation of quitenine, although a very careful search was made for hæmoquinic acid (compare A., 1919, i, 236; this vol., ii, 456).

J. C. D.

**The Transformations of Cinchonine.**

E. JUNGFLEISCH and E. LÉGER (*Ann. Chim.*, 1920, [ix], **14**, 59—128, 129—188).—A résumé of work already published (A., 1888, 380, 507, 612, 729, 969; 1889, 906; 1891, 1121; 1892, 222, 1253; 1893, i, 679; 1894, i, 262, 351; 1895, i, 310, 404; 1901, i, 287, 338; 1918, i, 121, 182, 232, 304; 1919, i, 170, 451, 597).

W. G.

**Syntheses of Inactive Ephedrine or  $\psi$ -Ephedrine.**

AUGUST EBERHARDT (*Arch. Pharm.*, 1920, **258**, 97—129).—Basing his experiments on the formula  $\text{OH}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{NHMe}$  proposed by Schmidt for the alkaloids, the author has succeeded in synthesising inactive ephedrine and  $\psi$ -ephedrine (which have not up to the present been obtained from the natural active bases) in such quantity that their resolution can now be studied; the method finally adopted is an improvement of that proposed by Schmidt and Calliess (A., 1911, i, 742).

*Methylation of Phenyl  $\alpha$ -Aminoethyl Ketone or Phenylaminoethylcarbinol.*—Phenylaminoethylcarbinol hydrochloride is slowly converted by methyl sulphate at  $100^\circ$  into a substance, shining needles and leaflets, m. p.  $244^\circ$ , which appears to have the constitution indicated by the formula  $\begin{array}{c} \text{CHPh}\cdot\text{CHMe}\cdot\text{NH}^3 \\ \text{O} \text{---} \text{SO}_2 \text{---} \text{O} \end{array}$ , and to be

analogous to the products obtained by Schmidt (A., 1914, i, 989) by the action of sulphuric acid on ephedrine and silver sulphate on  $\psi$ -ephedrine. Various attempts to methylate the free base with methyl sulphate are described, which, however, are either completely unsuccessful or yield such small amounts of methylated substance that its identity cannot be established. Similarly, the action of methyl sulphate on phenyl  $\alpha$ -aminoethyl ketone proceeds very indefinitely, but does not give rise to a betaine-like derivative, for the formation of which the presence of a hydroxyl group in the parent molecule appears to be necessary. Phenylaminoethylcarbinol hydrochloride is unaffected by methyl alcohol at  $170$ — $180^\circ$ . The main product of the action of methyl iodide on phenyl  $\alpha$ -aminoethyl ketone is diphenyldimethylpyrazine, needles, m. p.  $125^\circ$ , the decomposition of the ketone proceeding far more rapidly than its methylation; the substance is further identified by conversion into its unstable hydrochloride, platinichloride, aurichloride, yellow leaflets, m. p.  $115^\circ$ , mercurichloride, plates and flat needles, m. p.  $193$ — $195^\circ$  after softening at  $180^\circ$ , and its compound with silver nitrate,  $\text{C}_{18}\text{H}_{16}\text{N}_2\cdot 2\text{AgNO}_3$ , slender, shining needles, m. p.  $247^\circ$  (decomp.). Methyl iodide appears to be without action on the *acetyl* derivative of phenylaminoethyl-

carbinol or on mono- or di-benzoylphenylaminoethylcarbinols [the latter has m. p.  $165^{\circ}$  instead of  $162^{\circ}$ , recorded previously (A., 1917, i, 392), and yields a *hydrochloride*, needles, m. p.  $203^{\circ}$  after previous softening]. A satisfactory methylation could not be effected by the action of formaldehyde on phenylaminoethylcarbinol hydrochloride. Phenyl  $\alpha$ -aminoethyl ketone does not react readily with benzaldehyde, whilst the product obtained from phenylaminoethylcarbinol under similar conditions could not be caused to crystallise; treatment of the crude product with methyl iodide, however, gave a small quantity of phenylmethylaminoethylcarbinol hydriodide, plates, m. p.  $169$ — $170^{\circ}$ , which was further characterised by its conversion into the corresponding aurichloride, m. p.  $111.5^{\circ}$  after softening at  $108^{\circ}$ .

*Syntheses from Methylamine and Phenyl Bromoethyl Ketone.*— $\alpha$ -Methylaminopropiophenone is more conveniently prepared from methylamine and phenyl bromoethyl ketone in absolute alcoholic solution than in benzene solution, as previously described (A., 1915, i, 834), and is isolated as the hydrochloride; the latter is readily reduced by hydrogen under slight pressure in the presence of palladinised charcoal to phenyl- $\alpha$ -methylaminoethylcarbinol, m. p.  $114^{\circ}$ , the process being much preferable to the reduction with sodium amalgam described previously (*loc. cit.*); the hydrochloride thus obtained differs from the former compound in its higher melting point,  $187^{\circ}$  instead of  $181$ — $182^{\circ}$ , and its more sparing solubility. It is further found that, in addition to the compound, m. p.  $114^{\circ}$ , an isomeric substance, slender needles, m. p.  $76^{\circ}$ , also exists, and these are provisionally termed base *B* and base *A*. They yield, respectively, the *hydrochlorides*, readily soluble, ill-defined crystals, m. p.  $158$ — $161^{\circ}$ , and colourless, rhombic plates, m. p.  $187^{\circ}$ ; *aurichlorides*, flat needles, m. p.  $115$ — $116^{\circ}$ , and then yellow plates or golden-yellow lamellæ, m. p.  $115^{\circ}$ ; *platinichlorides*, reddish-yellow crusts, m. p.  $177^{\circ}$  (decomp.), and yellowish-red rosettes, m. p.  $183^{\circ}$  (decomp.); *dibenzoyl* derivatives, coarse, colourless crystals, m. p.  $118$ — $119^{\circ}$ , and colourless rods, m. p.  $114$ — $115^{\circ}$ . The *acetyl* derivative from either isomeride is oily, but yields a crystalline *hydrochloride*, colourless plates, m. p.  $165$ — $167^{\circ}$ .

The synthetic compounds, their salts, and derivatives show great similarity to the natural bases, both in appearance and melting point, which is particularly noticeable in the case of the *B*-base and  $\psi$ -ephedrine. The bases *A* and *B* exhibit an interconvertibility which is precisely similar to that of ephedrine and  $\psi$ -ephedrine. This can be partly effected by hydrochloric acid at the ordinary pressure, but more readily at higher temperature and under increased pressure, whilst the base *A* is completely converted into base *B* by acetylation—an action which is not observed during benzoylation. Transformation does not take place when base *A* is heated alone in the presence of alkali or of a number of solvents; with chloroform, the hydrochloride is formed as a result of the decomposition of the solvent.

H. W.

**Alkylation of Phenols with Benzenesulphonic Esters. Certain New Morphine Ethers.** ZOLTÁN FÖLDI (*Ber.*, 1920, 53, [B], 1839—1847).

The use of arylsulphonic esters for the conversion of phenols into ethers has been recommended by Ullmann and Wenner (*A.*, 1903, i, 407), but the optimal conditions for the reaction, and the influence on it of the presence of substituents in the phenol, do not appear to have been studied extensively. The author has therefore performed a series of experiments in which the phenol is generally dissolved in ethyl or amyl alcohol, treated with a solution of the calculated amount of sodium in one of these media, and the product is heated to boiling with the arylsulphonyl ester. The yields usually approximate to those theoretically possible, and since the alkylating agent is readily prepared (compare this vol., i, 828), the process appears capable of extended application. Alkylation occurs most readily with allyl benzenesulphonate, whilst the halogenated alkyl esters react considerably more slowly than the corresponding unsubstituted compounds. In general, it appears that the most easily saponifiable esters have the greatest alkylating action. With regard to substituents in the phenolic group, the same rule is applicable as in the case of alkylation with methyl sulphate; the presence of negative substituents hinders the reaction, but the effect is less marked with para- than with ortho-substituents.

The following ethers have not been described previously: *o*-chlorophenyl allyl ether, colourless oil, b. p. 118—120°/18 mm.,  $D_4^{15}$  1·133; catechyl diallyl ether, pale yellow, mobile oil, b. p. 140—145°/17 mm., 136—139°/14 mm.,  $D_4^{15}$  1·011; catechol mono-allyl ether, pale yellow, mobile liquid, b. p. 110°/12 mm.,  $D_4^{15}$  1·091; allylmorphine, colourless crystals (+ $\frac{1}{2}$ H<sub>2</sub>O), m. p. 67—68° [hydrochloride (+1H<sub>2</sub>O), m. p. 128—129° when rapidly, 130—132° when slowly heated, or anhydrous, m. p. 152—153°,  $[\alpha]_D^{19}$  -85·69° in aqueous solution; hydriodide, pale yellow, anhydrous crystals, m. p. 225—226°; normal sulphate, colourless needles (+3H<sub>2</sub>O), m. p. 167—168°, or anhydrous, m. p. 172—173°; hydrogen sulphate, m. p. 202—203°; normal phosphate, brownish-yellow powder, m. p. 100°, which, when crystallised from alcohol with addition of acetone and ether, passes into the dihydrogen phosphate, m. p. 186°; normal oxalate, m. p. 123° and 202—203° (after re-solidification)]; morphine  $\beta$ -chloroethyl ether, colourless crystals, m. p. 75—76° (+ $\frac{1}{2}$ H<sub>2</sub>O), 118—120° (anhydrous) [hydrochloride, m. p. 150—151° (+H<sub>2</sub>O), 166—168° (anhydrous); hydriodide, yellow crystals, m. p. 212—213°; normal sulphate, needles, m. p. 115—120° (effervescence), and subsequently 235—240° (decomp.); dihydrogen phosphate, coarse crystals, m. p. about 110° (effervescence); normal oxalate, slender needles, m. p. 85—87°]; morphine  $\beta$ -bromoethyl ether, m. p. 135—136° (effervescence), and subsequently 185—187°, is prepared in poor yield; attempts to prepare pure morphine  $\beta\beta$ -dichloroisopropyl ether were, as expected, unsuccessful.

H. W.

k k\*



**The Constitution of Surinamine.** E. WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1919, **107**, 314—315. Compare A., 1919, i, 415).—The author points out the advantage of preparing surinamine by E. Fischer and W. Lipschitz's method from tyrosine.  
S. S. Z.

**Modification of Skraup's Quinoline Synthesis.** EDWARD DE BARRY BARNETT (*Chem. News*, 1920, **121**, 205—206).—By a modification of Skraup's quinoline synthesis, using the aniline and glycerol in approximately equimolecular proportions, and calcined ferric oxide instead of nitrobenzene or arsenic acid as oxidising agent, yields of 40—50% of the theoretical, calculated on both aniline and glycerol, were obtained. Increasing the proportion of glycerol did not materially improve the yield of quinoline, and it seems probable that the comparatively low yield is due more to the destruction of the aniline by the oxidising agent than to the decomposition of the glycerol, as neither the addition of boric acid nor the employment of diluted sulphuric acid or a lower temperature appreciably altered the course of the reaction. A 60% yield of quinoline was, however, obtained by mixing 50 grams of aniline, 65 grams of glycerol, and 100 grams of ferric oxide, and adding the mixture rapidly to 150 c.c. of sulphuric acid in an open dish. After keeping for half an hour, the product was worked up in the usual way. The possibility of adapting a catalytic process to the synthesis by using a small quantity of ferric oxide or stannic sulphate and oxygen gas under pressure is discussed, and indications were obtained that on a large scale the process might be successful.  
G. F. M.

**Completely Methylated Quinic Acid.** J. HERZIG and HEDWIG ORTONY (*Arch. Pharm.*, 1920, **258**, 91—96).—Exceptional difficulties have previously been encountered in methylating quinic acid; it is now found, however, that it is slowly converted into *methyl tetramethylquinat*e, rhombic crystals,  $a:b:c=0.6741:1:0.5960$ , m. p. 56—58°,  $[\alpha]_D -18.5^\circ$  in benzene solution, by repeated treatment with methyl iodide and silver oxide; the ester decomposes to some extent when distilled in a vacuum. Attempts to hydrolyse it by alkali or by aqueous hydrochloric acid did not proceed smoothly, a portion of the ester remaining unattacked, whilst another portion lost the ethereal methoxy-groups to a greater or less extent. Oxidation with chromic acid in acetic acid solution, or with potassium permanganate in alkaline solution, yields a mixture of unchanged ester and highly oxidised substances. It is not readily dehydrogenated by iodine. Attempts to effect methylation with methyl iodide and methyl alcohol in the presence or absence of a little copper or gold were not more successful. The action of diazomethane is rapid at first, but subsequently very slow, so that the preparation of a completely methylated product in this manner is very difficult, if at all possible.

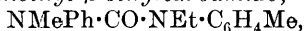
The application of Purdie's method to other cases of difficult methylation has also been investigated. 2:4:6-Trihydroxy-

1:1:2:3:3:4:5:5:6-nonamethylcyclohexane (Herzig and Erthal, A., 1911, i, 778) is fairly readily converted into a monomethoxy-derivative (which could not be isolated in the pure state, owing to lack of material), but a further marked increase in the methoxy-content is not effected by eleven successive treatments of the product with methyl iodide and silver oxide. Quercitol could not be methylated under widely varied conditions.

It does not appear possible to replace the silver oxide by lead oxide.

H. W.

**Preparation of Diaryldialkylcarbamides.** FABRIQUES DE PRODUITS DE CHIMIE ORGANIQUE DE LAIRE (D.R.-P. 323534; from *Chem. Zentr.*, 1920, iv, 437—438).—The carbamyl chloride obtained from alkylated *o*-toluidine is brought into reaction with an alkylated aryl amine or alkylated *o*-toluidine, and is caused to react with the carbamyl chloride derived from another alkyl aryl amine. Thus, carbonyl chloride and ethylaniline yield *phenyl-ethylcarbamyl chloride*,  $\text{NPhEt}\cdot\text{COCl}$ , m. p. about  $50^\circ$ , which, with methyl-*o*-toluidine, gives  $\alpha$ -phenyl- $\beta$ -*o*-tolyl- $\beta$ -methyl- $\alpha$ -ethylcarbamide,  $\text{NEtPh}\cdot\text{CO}\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\text{Me}$ , b. p.  $180\text{--}190^\circ/20\text{--}22\text{ mm.}$ ,  $210\text{--}220^\circ/30\text{--}32\text{ mm.}$ , and miscible in all proportions with the common organic solvents and with collodion. Similarly, *phenyl-methylcarbamyl chloride*, m. p.  $88^\circ$ , and ethyl-*o*-toluidine give  $\alpha$ -phenyl- $\beta$ -*o*-tolyl- $\alpha$ -methyl- $\beta$ -ethylcarbamide,



b. p.  $212\text{--}220^\circ/25\text{--}27\text{ mm.}$  *Di-*o*-tolylethylmethylcarbamide*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NEt}\cdot\text{CO}\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\text{Me}$ , from *o*-tolylethylcarbamyl chloride and methyl-*o*-toluidine, has m. p.  $40\text{--}42^\circ$ , b. p.  $205\text{--}215^\circ/23\text{ mm.}$  The carbamides absorb nitrous fumes, and are expected to find application as binding agents for nitrocellulose in the preparation of explosives and celluloid.

H. W.

**Preparation of an Arylcarbamide.** J. D. RIEDEL, AKT.-GES., (D.R.-P. 323298; from *Chem. Zentr.*, 1920, iv, 437).—Ethylene chlorohydrin is allowed to react with *p*-nitrophenol, and the product, after being reduced to the corresponding amine, is transformed into the carbamide in the usual manner. *p*-Nitrophenyl hydroxyethyl ether crystallises in pale yellow needles, m. p.  $94\text{--}95^\circ$ . *p*-Aminophenyl hydroxyethyl ether hydrochloride, needles, m. p.  $204\text{--}205^\circ$ , is converted by aqueous potassium cyanate into the corresponding carbamide, m. p.  $159\text{--}160^\circ$ .

H. W.

**The Action of Pyrrolidonecarboxyl Chloride on Leucine Ethyl Ester.** EMIL ABDERHALDEN and HANS SPINNER (*Zeitsch. physiol. Chem.*, 1919, 107, 1—6).—The pyrrolidonecarboxyl leucine ester described by Abderhalden and Wurm (A., 1913, i, 90) is found to be a mixture. The pure ester was prepared by treating a chloroform solution of *dl*-leucine ethyl ester with *dl*-pyrrolidonecarboxyl chloride. After distilling off the chloro-

form, the syrup was extracted with absolute alcohol, and the chlorine removed by adding a calculated quantity of sodium and precipitating with alcohol. The filtrate was evaporated in a vacuum at 35–40°, and extracted with light petroleum. The residue was then dissolved in ethyl acetate. This solution, on concentration, yielded small, colourless needles, which, on purification, was found to be *glutaminyl leucine ethyl ester*,  $C_{13}H_{24}O_5N_2$ , m. p. 120–122°. The filtrate, on being further concentrated, yielded an orange-red syrup and oblong leaflets. The syrup was extracted with ether, and the leaflets were collected and found to be *pyrrolidonecarboxyl leucine ethyl ester*,  $C_{13}H_{24}O_4N_2$ , m. p. 147–148°. 1-Leucine methyl ester was prepared by treating L-leucine ( $[\alpha]_D^{25} + 15.83^\circ$ ) suspended in methyl alcohol with hydrogen chloride, and then boiling for half an hour. The methyl alcohol was removed by distillation in a vacuum, and the residue dissolved in water. The aqueous solution was then extracted with ether in the presence of sodium hydroxide, and from the extract, after removal of the ether, the ester remained, b. p. 79–79.5°/12 mm.,  $D^{17} 0.9533$ ,  $[\alpha]_D^{17} + 16.52^\circ$ . S. S. Z.

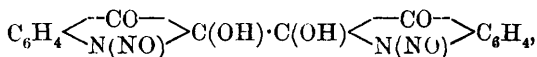
**Organic Disulphides.** FRITZ VON KONEK (*Ber.*, 1920, **53**, [B], 1666–1671).—In connexion with Lecher's recent communication on the valency problem of sulphur (this vol., i, 433), the author gives a more extended account of antipyrine and homoantipyrine (1-phenyl-3-methyl-2-ethylpyrazolone) disulphides, a short notice of which has appeared previously (*A.*, 1911, i, 505). Although no new experimental evidence is adduced, the constitution of the compounds has become more obvious in the light of more recent research, and they are now regarded as symmetrical disulphides. The readiness with which they react with mercury when dissolved in chloroform and yield mercaptides is, however, very remarkable, particularly as Lecher has found that the various disulphides examined by him have but little tendency to dissociate into radicles, even at high temperatures. Since the disulphides of antipyrine and homoantipyrine exhibit a normal molecular weight in boiling alcohol, and therefore cannot possibly be dissociated into radicles containing univalent sulphur, the author is led to the conclusion that their smooth and quantitative transformation into mercaptides in cold chloroform solution is to be attributed to a dissociation into radicles, which only occurs under the influence of the chemical affinity of mercury for sulphur in the first moments of the action, and that this is immediately followed by union of the nascent radicles through the mercury bridge. H. W.

**Action of Nitrous Fumes on Indigotin.** THEODOR POSNER and GÜNTHER ASCHERMANN (*Ber.*, 1920, **53**, [B], 1925–1940).—Indigotin, when suspended in ethyl alcohol and treated with nitrous fumes, is gradually decolorised and dissolved, with the formation of ethyl phenylglyoxylate. In order to elucidate the probable course of the reaction, the behaviour of indigotin, when

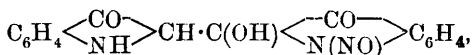
similarly treated in the presence of a number of solvents, has been investigated, and it is thus shown that the intermediate products are derivatives, not of dehydroindigotin (compare Kalb, A., 1909, i, 966; 1910, i, 340; 1912, i, 725), but of dihydroindigotin.

Ethyl phenylglyoxylate, obtained from indigotin and nitrous fumes in the presence of ethyl alcohol (96%) at the ordinary temperature, has b. p. 138—139·2° (corr.)/12 mm., 263·6—264·6°/756 mm. (corr.; slight decomp.), and is further identified by hydrolysis to phenylglyoxylic acid, m. p. 61—63°, and conversion of the latter into its phenylhydrazone, m. p. 163°. In the presence of methyl alcohol, *methyl phenylglyoxylate*, yellow, almost odourless liquid, b. p. 136·8—137·2° (corr.)/14 mm., 254·6—255·6° (corr.)/756 mm., is produced; if the reaction is interrupted before it is complete, unchanged indigotin and isatin can also be isolated.

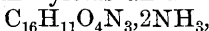
The action of nitrous fumes on a suspension of indigotin in ether causes the separation of *dinitrosodihydroxydihydroindigotin*,



yellow powder, which can be preserved for several days when perfectly pure, but, in its crude state, readily decomposes, frequently with spontaneous ignition; it becomes decomposed when slightly warmed; the mother liquors from its preparation evolve nitrous fumes and carbon monoxide violently when warmed, and yield benzoic acid. It is transformed by ethyl alcohol at 40—55° into *nitrosohydroxydihydroindigotin*,



almost colourless, crystalline powder, m. p. 194° (decomp.) after darkening at about 190°, together with small amounts of isatin. The mononitroso-compound yields an *ammonium* salt,

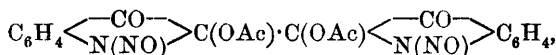


colourless powder, m. p. 168—170° (decomp. above 140°), and is transformed by uncooled methyl alcohol and nitrous fumes into methyl phenylglyoxylate. It is converted by boiling acetic anhydride into a mixture of *nitrosohydroxydihydroindigotin*

*acetate*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{C(OH)} \\ \text{<N}^+\text{Ac}^- \end{array} \text{C·C(OH)} \begin{array}{c} \text{---CO---} \\ \text{<N(NO)} \end{array} \text{C}_6\text{H}_4$ , yellow crystals, m. p. 275—278° after darkening at 265°, and *dihydroxydihydroindigotin diacetate*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{C(OH)} \\ \text{<N}^+\text{Ac}^- \end{array} \text{C·C(OH)} \begin{array}{c} \text{CO} \\ \text{<N}^+\text{Ac}^- \end{array} \text{C}_6\text{H}_4$ ,

yellow powder, m. p. above 325° after darkening at 310°, which is insoluble in all the commoner media.

*Dinitrosodihydroxydihydroindigotin diacetate*,

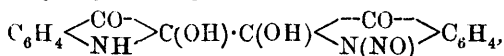


pale yellow, crystalline powder, m. p. 172° (decomp.) when rapidly heated, is prepared by the action of nitrous fumes on indigotin suspended in acetic acid; the substance cannot be pre-

served for any length of time. It is slowly converted by boiling ethyl alcohol into isatin and ethyl phenylglyoxylate, very rapidly by boiling glacial acetic acid into nitrosohydroxydihydroindigotin, m. p. 190—194° (decomp.); it is reduced by zinc dust in the presence of acetic anhydride and sodium acetate to tetra-acetyl-indigo-white, m. p. 256°.

A suspension of isatin in ethyl alcohol is gradually converted by nitrous fumes into ethyl phenylglyoxylate.

The course of the action in ethyl-alcoholic solution therefore appears to be as follows: indigotin is converted into dinitroso-dihydroxydihydroindigotin, which is reduced by alcohol to nitroso-hydroxydihydroindigotin on the one hand and converted into nitrosodihydroxydihydroindigotin,



on the other. Part of the latter is reduced to nitrosohydroxydihydroindigotin, whilst another part is oxidised to isatin and *N*-nitrosoisatin,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{N}(\text{NO}) \end{array} \text{CO}$ . This compound unites with a molecule of alcohol, forming the diazohydrate of ethyl phenylglyoxylate,  $\text{HO} \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CO}_2\text{Et}$ , which is subsequently reduced by alcohol to phenylglyoxylic ester. H. W.

**The Acenaphthene Series. I. The Conversion of *o*-Nitroamines into *iso*Oxadiazole Oxides.** FREDERICK MAURICE ROWE and JOHN STANLEY HERBERT DAVIES (T., 1920, 117, 1344—1351).

**The Sulphonation of Glyoxalines.** FRANK LEE PYMAN and LEONARD ALLAN RAVALD (T., 1920, 117, 1429—1431).

**The Formation and Reactions of Imino-compounds. XX. The Condensation of Aldehydes with Cyanoacetamide.** JAMES NELSON EDMUND DAY and JOCELYN FIELD THORPE (T., 1920, 117, 1465—1474).

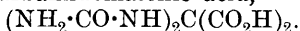
**Iminazoleisopiperidine [Tetrahydro-1 : 3 : 5-benzotriazole] and its Derivatives.** SIGMUND FRÄNKEL and KAROLINE ZEIMER (*Biochem. Zeitsch.*, 1920, 110, 234—244).—4- $\beta$ -Aminoethylglyoxaline was prepared by eliminating the carboxyl group of histidine hydrochloride by means of bacterial action. It was then treated with concentrated hydrochloric acid and methylal on the water-bath under a reflux condenser. The product of the reaction was freed from the hydrochloric acid by evaporation, and recrystallised from alcohol. The tetrahydro-1:3:5-benzotriazole hydrochloride thus obtained forms triclinic crystals, m. p. 253°. *Tetrahydro-1:3:5-benzotriazole*,  $\text{CH} \begin{array}{c} \text{NH} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{N} = \text{C} \cdot \text{CH}_2 \cdot \text{NH} \end{array}$ , obtained by treating the hydrochloride with silver carbonate, is crystalline, m. p. 110°. The

following derivatives were prepared: *dipicrate*,

$C_6H_9N_3(C_6H_3O_7N_3)_2$ ,  
m. p.  $220^\circ$ ; *dipicrolonate*,  $C_6H_9N_3(C_{10}H_8O_5N_4)_2$ , EtOH, m. p.  $250^\circ$ ;  
*aurichloride*,  $C_6H_9N_3AuCl_3$ , m. p.  $217^\circ$ ; *platinichloride*,

$C_6H_9N_3PtCl_6 \cdot H_2O$ ,  
decomp.  $280^\circ$ ; *mercurichloride*,  $C_6H_9N_3(HgCl_2)_4$ , m. p.  $210^\circ$ ;  
*N-acetyl-hydrochloride*,  $C_6H_8N_3Ac \cdot HCl \cdot H_2O$ , m. p.  $235^\circ$ ; *N-di-*  
*benzoyl* derivative,  $C_6H_7N_3Bz_2 \cdot H_2O$ , m. p.  $215^\circ$ . Hydroxyhydro-  
*isoquinoline* was prepared by treating tyramine with concentrated  
hydrochloric acid and methylal on the water-bath under the reflux  
condenser. S. S. Z.

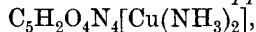
**Uroxanic Acid.** HEINRICH BILTZ and RUDOLF ROBL (*Ber.*, 1920, **53**, [B], 1950—1963).—Uroxanic acid has been largely investigated by Behrend (A., 1904, i, 950) and Behrend and Schultz (A., 1909, i, 272), and it has been shown that, in all probability, the substance is dicarbamidomalonic acid,



This view of its constitution has now been fully confirmed.

Potassium uroxanate is moderately rapidly obtained by the oxidation of a solution of uric acid in an excess of aqueous potassium hydroxide by purified air at  $38^\circ$ , and very slowly prepared in a similar manner at the ordinary temperature; the oxidation is, however, more conveniently effected with aqueous potassium permanganate, the yield being 27% of that theoretically possible (allantoin is also formed). The salt forms colourless crystals,  $a:b:c=0.88576:1:1.2044$ , and gives hydrates containing 3.5, 3, and probably also 0.5  $H_2O$ . Uroxanic acid crystallises in indistinct tetrahedra, decomp.  $162^\circ$  [the sodium salt, hexagonal leaflets (+  $8H_2O$ ), decomp.  $182^\circ$  [the sodium salt, hexagonal leaflets (+  $8H_2O$ ), decomp.  $182^\circ$  after becoming discoloured at about  $172^\circ$ , and the *silver* salt, colourless, crystalline powder, are described]. Uroxanic acid is reduced by fuming hydriodic acid to hydantoin, and, hydrolysed by warm water (with loss of carbon dioxide), to carbamide and "glyoxyl-carbamide," decomp.  $120-125^\circ$  (compare following abstract), the latter change being also effected by concentrated nitric acid. Cold dilute hydrochloric acid transforms it into allantoin, whilst *spiro-dihydantoin* (A., 1917, i, 290) is formed under similar conditions with concentrated hydrochloric acid.

Esterification of the carboxy-groups of uroxanic acid cannot be effected with methyl alcohol and hydrogen chloride, with methyl sulphate in alkaline solution, or from the silver salt and methyl iodide; with the aid of diazomethane, however, it has been found possible to prepare *methyl uroxanate*, decomp.  $213^\circ$ , which is slowly hydrolysed to uroxanic acid by aqueous potassium hydroxide solution, and converted by boiling water into *spiro-dihydantoin*, which is conveniently identified as the di-silver salt,  $C_5H_2O_4N_4Ag_2 \cdot 2H_2O$ , and the *diammine copper* salt,



pale blue, matted needles.

The presence of the two carbamido-groups is deduced from the behaviour of the substance towards nitrous acid, which, under definite conditions (see later), leads to the quantitative evolution of the whole of the nitrogen. It is shown at the instance of uric acid, uric acid glycol, methyl urate, hydantoin, glyoxylcarbamide, and alloxanic acid that nitrogen united in a ring is not liberated by nitrous acid in these circumstances, whilst, on the other hand, the nitrogen of primary amines and of substances which contain the carbamido-group as an open chain, and in which an alkyl group is not attached to the nitrogen atom, is evolved in the free state. Whilst the former statement appears to be universally true, the latter is subject to certain exceptions, since, although it is valid in the cases of methylamine hydrochloride, glycine, leucine, carbamide, *as*-dimethylcarbamide, allantoic acid, and 1:3:7-trimethyl- $\psi$ -uric acid, it does not hold for certain methylated allantoinins in which the expected decomposition does not occur, nor for derivatives of carbamide containing negative substituents (acetylcarbamide, benzoylcarbamide, allophanic ester,  $\psi$ -uric acid, 5-methoxy- $\psi$ -uric acid), which are not decomposed. For the estimation of the nitrogen, a weighed quantity of the substance is placed with about 1 gram of solid sodium nitrite in a flask through which a current of carbon dioxide can be passed, and provided with a dropping funnel, and connected through bulbs containing a solution of chromium trioxide (100 grams) in nitric acid (12%; 100 c.c.) to a nitrometer filled with potassium hydroxide solution. The apparatus is filled with carbon dioxide, and sodium nitrite solution (40%; 20 c.c.) is admitted, followed by 2*N*-sulphuric acid, the rate of addition of the latter being so controlled that the solution retains a green colour and evolves oxides of nitrogen. After completion of the action, the residual nitrogen is driven into the nitrometer by carbon dioxide.

Elimination of the carbamido-groups from uroxanic acid by means of sodium nitrite leads to the formation of mesoxalic acid.

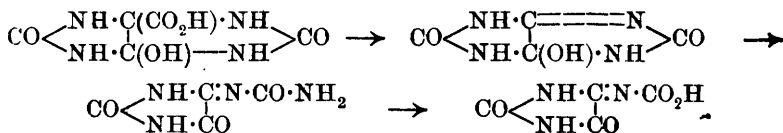
H. W.

**Mechanism of the Formation of Uroxanic Acid from Uric Acid.** HEINRICH BILTZ and FRITZ MAX (*Ber.*, 1920, 53, [B], 1964—1966).—It can scarcely be doubted that the primary product of the oxidation of uric acid in alkaline solutions contains two hydroxyl groups in the 4:5-positions, but all attempts to prepare uroxanic acid directly from the uric acid-4:5-glycol have failed. It is now shown, however, that it can be obtained when the corresponding dimethyl ether is gently warmed with dilute alkali. It is therefore quite possible that the formation of the glycol is the first step in the conversion of uric into uroxanic acid, but that the spatial configuration of the intermediate glycol differs from that of the isolated compound. The further action probably proceeds either through *spiro*dihydantoin or hydroxydicarbamidoethane-carboxylic ester,  $\text{CO} < \begin{array}{c} \text{NH} \cdot \text{C}(\text{CO}_2\text{R}) \cdot \text{NH} \\ \text{NH} \cdot \text{C}(\text{OH}) \cdot \text{NH} \end{array} > \text{CO}$ ; the former has been shown to be convertible into uroxanic acid (Biltz and Heyn, A.,

1917, i, 290), but, for other reasons, the authors consider the latter to be the more probable intermediate substance. H. W.

**Oxonic Acid.** HEINRICH BILTZ and RUDOLF ROBL (*Ber.*, 1920, 53, [B], 1967—1983).—Oxonic acid in the form of its potassium, potassium hydrogen, sodium, ammonium hydrogen, and barium hydrogen salts was isolated by Strecker from the products of the slow oxidation of alkaline solutions of uric acid by air, and the account of the work was published after Strecker's death by Medicus (this Journ., 1875, 555). Since then, very little progress has been made with the investigation of the substance, largely owing to its difficult accessibility. The present authors find that potassium hydrogen oxonate can be rapidly prepared by addition of finely divided potassium permanganate to a solution of uric acid in an excess of aqueous potassium hydroxide at 30—40°, followed by cautious addition of acetic acid. The identity of the oxonic acid derivatives obtained in this manner with Strecker's preparation is established by comparison of a series of salts. A further advance is made through the observation that free *oxonic acid*, platelets (+ 2H<sub>2</sub>O), can be obtained by the action of hydrochloric acid (10%) on the potassium hydrogen salt; as is to be expected, it is very unstable, and evolves carbon dioxide when treated with water at 40°, passing thereby into a substance, which Strecker merely designates "new acid from oxonic acid," but Medicus (*loc. cit.*)

describes as "crystalline glyoxylurea,"  $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CH} \cdot \text{OH} \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$ . Complete analyses of this substance have shown that this formula is incorrect, and that it actually has the composition C<sub>3</sub>H<sub>3</sub>O<sub>2</sub>N<sub>3</sub>, and is identical with allantoxaidin, which has been prepared by Mulder (A., 1871, 1197) and van Embden (this Journ., 1873, 1025) by the oxidation of allantoin by potassium ferricyanide in alkaline solution, and the constitution of which has been elucidated by Ponomarew (A., 1879, 226). Oxonic acid is therefore identical with allantoxanic acid,  $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{C} \cdot \text{N} \cdot \text{CO}_2\text{H} \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$ . Its production from uric acid is explained according to the scheme: uric acid →



The work described in this and the preceding abstracts allows a fairly complete picture to be drawn of the oxidation of uric acid in alkaline solution. If the latter is concentrated and cooled, potassium uroxonate separates; if it is acidified with acetic acid (particularly after addition of alcohol), potassium hydrogen oxonate crystallises, whilst if the acidified solution is preserved or evaporated and cooled, allantoin is obtained.

The following substances are described: *methyl oxonate*, viscous



syrup, which could not be caused to crystallise; *normal potassium oxonate*,  $C_4H_4O_4N_3K_2 \cdot H_2O$ ; *zinc hydrogen oxonate*, thin platelets ( $+4H_2O$ ); *normal lead oxonate*, small, rhombic crystals; *normal silver oxonate*, voluminous precipitate; the silver salt, dense, white precipitate; *hydrazine salt*, slender needles, m. p.  $204^\circ$ , and *phenylhydrazine salt*, pale yellow leaflets, m. p.  $228^\circ$  (decomp.), of allantoxaidin.

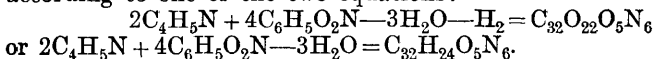
A solution of oxonic acid is almost quantitatively oxidised to cyanuric acid by potassium permanganate in the presence of sulphuric acid.

Dehydrated allantoxaidin is converted by an ethereal solution of diazomethane into *dimethylallantoxaidin*, short prisms, m. p.  $158^\circ$ ; the same compound is obtained from the silver salt of allantoxaidin and methyl iodide. Both methyl groups are attached to nitrogen. Dilute mineral acids decompose allantoxaidin into formic acid and biuret; concentrated nitric acid causes a similar decomposition, yielding, however, 1-nitrobiuret, decomp.  $165^\circ$ .

Ponomarew's synthetic production of oxonic acid (allantoxanic acid) from parabanic acid and carbamide is confirmed; similarly, methylparabanic acid and carbamide give an amorphous, yellow condensation product, decomp. ca.  $200^\circ$ , which is converted by potassium hydroxide into a crystalline *potassium salt*, yielding (?) *methyloxonic acid*, decomp.  $135^\circ$ . On the other hand, dimethylparabanic acid could not be condensed with carbamide, methylcarbamide, or *s*- or *as*-dimethylcarbamide. H. W.

**Pyrrole-blacks.** VIII. A. ANGELI and C. LUTRI (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 420—423. Compare this vol., i, 397).—A black substance identical in composition and properties with that obtained by the interaction of pyrrole and *p*-benzoquinone in presence of water is formed when this reaction takes place in acetic acid solution. It is therefore probable that this substance represents an individual compound, and it is assumed that, in its formation, the quinonoid and pyrrole rings unite.

When treated with nitrous acid, pyrrole yields intensely black products (compare Angeli and Cusmano, A., 1917, i, 413), and it is now found that the interaction of pyrrole and *p*-nitrosophenol in cold acetic acid gives an amorphous, deep violet-black powder insoluble in the ordinary solvents, but soluble in alkalis, giving black solutions; this powder has a composition corresponding with the formula  $C_{32}H_{22}O_5N_6$  or  $C_{32}H_{24}O_5N_6$ , and appears to be formed according to one of the two equations:



Intensely coloured products are formed also by the action of pyrrole on *p*-quinoneimine or *p*-quinonedi-imine. T. H. P.

**Catalytic Reduction of *o*-Nitroazoxybenzene.** GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 93—95).—When an ethereal solution of *mm'*-dinitroazoxybenzene, contain-

ing platinum-black in suspension, is shaken at the ordinary temperature in an atmosphere of hydrogen, the gas is rapidly absorbed, with formation of various reduction products, principally *o*-aminoazoxybenzene,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{NPh} : \text{O}$ , which crystallises in long, flattened prisms, m. p.  $97^\circ$ , forms colourless, well-crystallised salts with hydrochloric and sulphuric acids, and yields an *acetyl* derivative, m. p.  $157^\circ$ . When heated on a boiling-water bath with concentrated sulphuric acid, it does not undergo Wallach's transposition, according to which azoxybenzenes are converted into the isomeric hydroxyazo-compounds, but it suffers intramolecular dehydration, with formation of 2-phenyl-1:2:3-benzotriazole,  $\text{C}_6\text{H}_4 \cdot \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} > \text{NPh}$  or  $\text{C}_6\text{H}_4 \cdot \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} > \text{NPh}$ . The detailed results are to be published later.

T. H. P.

### Electrolytic Reduction of Hydroxyazo-compounds. II.

E. PUXEDDU (*Gazzetta*, 1920, **50**, ii, 149—159. Compare A., 1918, i, 551).—Further experiments on the electrolytic reduction of hydroxyazo-compounds, mostly in acid solution, show that such reduction always consists in rupture of the azo-linking, with formation of two bases, namely, the aniline used to prepare the hydroxyazo-compound and the aminophenol, corresponding with the phenol used in this preparation; no other reduction products have been isolated.

In presence of sodium hydroxide, the electrolytic reduction of *p*-benzeneazophenol proceeds with difficulty, and gives poor yields. In acid solution, 3-benzeneazo-*o*-cresol yields aniline and 5-amino-*o*-cresol, but in alkaline solution only the aniline is detectable. Other compounds investigated were 4-*o*-tolueneazophenol and 4-*p*-tolueneazophenol.

T. H. P.

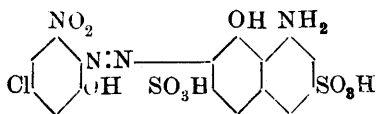
**Diazotisation of Polynitroanilines.** EMIL MISSLIN (*Helv. Chim. Acta*, 1920, **3**, 626—639).—The loosening influence which the diazo-group exerts on ortho-substituents is enhanced, especially by negative groups in the para-position, and this becomes of importance if the behaviour of more highly negatively substituted dinitroanilines on diazotisation is to be studied. Up to the present, picramide has been regarded as incapable of diazotisation, as it does not yield to the methods usually employed to meet such cases. Even with 4-chloro-2:6-dinitroaniline, it is easily seen that the diazonium compound, obtained by treatment of its concentrated sulphuric acid solution with nitrosylsulphuric acid in the cold, loses increasing amounts of nitrous acid after being poured into ice-water and allowed to remain, the power of coupling with  $\beta$ -naphthol also diminishing; it is found that one of the nitro-groups undergoes replacement by hydroxyl.

Similar, but still more pronounced, behaviour is shown by a diazotised solution of 2:6-dinitroaniline-4-sulphonic acid in concentrated mineral acid; this is stable, but, on neutralisation with sodium acetate or sodium hydrogen carbonate, an ortho-nitro-group is eliminated and replaced by hydroxyl.

As regards the properties which must be shown by diazotised 2:4:6-trinitroaniline solutions, Witt's assumption that amines such as this, which are unable to form salts, are absolutely undiazotisable (A., 1909, i, 855), is beside the mark, since the solution of this amine in concentrated sulphuric acid undoubtedly contains picramide sulphate. There is hence no ground for assuming that picramide cannot be diazotised, the only necessary condition being the exclusion during the process of diazotisation of the hydrolysing action of water, which is indirectly the cause of the loosening influence of the diazo-group.

On these considerations is based the following method for diazotising di- and tri-nitroanilines of the type of picramide. The amine is dissolved in glacial acetic acid and the solution treated carefully in the cold with nitrosylsulphuric acid or with a solution of sodium nitrite in sulphuric acid monohydrate, the weight of the latter used in the case of trinitroanilines being equal to that of the acetic acid used for dissolving the amine. If much less sulphuric acid is taken, say 2 mols. per 1 mol. of amine, no diazotisation takes place, even in glacial acetic acid, excess of sulphuric or nitrosylsulphuric acid being evidently necessary to give the sulphate of the amine. By this method, 2:4:6-trinitroaniline, 2:4:6-trinitro-3-methoxyaniline, 2:4:6-trinitro-3-ethoxyaniline, and 2:4:6-trinitro-3-hydroxyaniline have been diazotised and coupled with  $\beta$ -naphthol to form colouring matters, the yield of the latter in the pure state amounting to 80%. Further, 2:4:6-trinitro-*m*-phenylenediamine has been tetrazotised by this method, but the diazotisability of 2:3:4:6-tetranitroaniline remains uncertain.

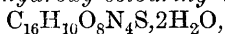
Diazotisation of 4-chloro-2:6-dinitroaniline, and coupling of the product with 1:8-aminonaphthol-3:6-disulphonic acid, yields the *colouring matter* (annexed formula), which crystallises in small, bronzed needles and exhibits the properties of a typical *o*-hydroxyazo-colouring matter; in a faintly acid bath, it



dyes wool bluish-Bordeaux, the colour being sensitive to acid, and yielding pure blue and violet-black tints when treated with copper sulphate and chromed respectively. With  $\beta$ -naphthol, the diazo-solution forms the *colouring matter*,  $C_{16}H_9O_5N_4Cl$ , which separates in stout, reddish-brown, shining crystals, dissolves in concentrated sulphuric acid to a violet-blue solution, and is precipitated from the latter unaltered by addition of water. Freshly prepared 4-chloro-2:6-dinitroaniline diazo-solution gives, with a solution of  $\beta$ -naphthol-6-sulphonic acid rendered alkaline with sodium carbonate, a colouring matter which colours wool yellowish-orange, and with 1:8-aminonaphthol-3:6-disulphonic acid in alkaline solution, a monoazo-colouring matter, which dyes wool bluish-Bordeaux, and in which the two nitro-groups in the ortho-positions to the amino-group still persist. The *colouring matter* formed by

coupling with  $\alpha$ -naphthol crystallises in slender, brownish-yellow, shining needles ( $+1\text{C}_2\text{H}_4\text{O}_2$ ), dissolves in concentrated sulphuric acid to a violet-blue solution, and is precipitated unchanged from the latter by addition of water. Typical for the  $\alpha$ -naphthol colouring matter is the property of dissolving in dilute sodium hydroxide solution to a deep blue solution, from which sodium or potassium chloride precipitates the corresponding salt in shining crystals resembling crystal-violet. This behaviour confirms the expectation that the union with  $\alpha$ -naphthol takes place in the para-position to the hydroxyl group; the  $\beta$ -naphtholazo-colouring matter is insoluble in cold aqueous sodium hydroxide. Noteworthy is the great affinity towards wool of the  $\alpha$ -naphthol product in dilute sodium hydroxide. The deep blue coloration is converted into orange by atmospheric carbon dioxide.

Diazotised 2:6-dinitroaniline-4-sulphonic acid gives with  $\beta$ -naphthol a typical  $\alpha$ -hydroxy-colouring matter,



which forms shining, brownish-orange needles, and in faintly acid bath colours wool bright orange; the coloration is sensitive to alkali, and is turned blue by ammonia, the colouring matter being destroyed by boiling with dilute sodium hydroxide. The corresponding  $\alpha$ -naphtholazo-colouring matter forms a brownish-yellow, crystalline powder, and in faintly acid solution produces on wool yellowish-brown tints, which are still more sensitive to alkali, being changed to deep blue, even by dilute sodium carbonate solution.

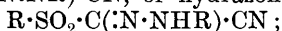
Diazotisation of picramide and coupling with  $\beta$ -naphthol yields the colouring matter,  $\text{C}_{16}\text{H}_9\text{O}_7\text{N}_5$ , which crystallises in greenish-blue, spear-like crystals with metallic lustre, or in shining, reddish-brown cubes; it dissolves in concentrated sulphuric acid, giving a blue solution. The corresponding  $\alpha$ -naphthol compound forms shining, yellowish-brown crystals, giving a violet-blue solution in concentrated sulphuric acid.

Diazotisation of 2:4:6-trinitro-3-hydroxyaniline and coupling with  $\beta$ -naphthol gives the colouring matter, which separates in brownish-black crystals with metallic lustre, and yields a blue solution in concentrated sulphuric acid and a Bordeaux solution in dilute sodium hydroxide solution; gentle heating of the alkaline solution destroys the colouring matter. 2:4:6-Trinitro-3-methoxy- (and ethoxy-) anilines yield similar compounds, and 2:4:6-trinitro-*m*-phenylenediamine the corresponding tetrazo-colouring matter.

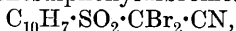
T. H. P.

**Action of Diazonium Salts on Arylsulphonated Aceto- and Propio-nitriles.** J. TRÖGER and R. WUNDERLICH (*J. pr. Chem.*, 1920, [ii], 101, 157—170. Compare A., 1905, i, 336, 870; 1908, i, 798; 1915, i, 792).—Arylsulphonated acetonitriles have been shown to differ in behaviour from arylsulphonated propionitriles, since they readily dissolve in alkali hydroxide solution, in which the latter are insoluble. Both classes of compounds are now shown to react with diazonium salts. The propionitrile

derivatives so obtained must necessarily be regarded as azo-compounds, but the acetonitrile derivatives may be either azo-compounds,  $R \cdot SO_2 \cdot CH(\cdot N : NR) \cdot CN$ , or hydrazones,



the latter assumption is the more probable, since the derivatives, like the parent substance, are soluble in alkali hydroxide solution. Attempts to adduce more definite evidence did not meet with success. Assuming the acetonitrile compound to be a true azo-derivative, it should pass, when methylated, into the corresponding propionyl compound; this does not appear to be the case, but the processes of methylation and purification of the methylated product are beset by unusual difficulties, so that trustworthy conclusions can scarcely be drawn. An attempt to prepare an undoubted hydrazone of an acetonitrile compound was made at the instance of  $\alpha$ -naphthalenesulphonyldibromoacetonitrile,



which, however, could not be induced to react with phenylhydrazine in the desired sense, the ultimate product being  $\alpha$ -naphthalenesulphonylacetonitrile.

The compounds are prepared either by the addition of the diazonium solution to a well-cooled solution of the nitrile in an excess of aqueous sodium hydroxide, followed by acidification with acetic acid, or by slowly running the diazonium solution into an alcoholic solution of the nitrile in the presence of saturated aqueous sodium acetate solution; only the second process is available in the case of the propionitrile derivatives.

The following compounds have been prepared:  $\alpha$ -naphthalenesulphonylacetonitrile, m. p. 111—112° (Tröger and Helle, *loc. cit.*, give 109°);  $\alpha$ -naphthalenesulphonylbenzeneazoacetonitrile or phenylhydrazone of  $\alpha$ -naphthalenesulphonylformyl cyanide, reddish-yellow, six-sided crystals, m. p. 203° [potassium salt (+ 3H<sub>2</sub>O), golden-yellow crystals; sodium salt, freely soluble in water, and not obtained in the crystalline state; lead salt, canary-yellow, amorphous precipitate; silver salt, canary-yellow precipitate];  $\alpha$ -naphthalenesulphonyl-p-tolueneazoacetonitrile or p-tolylhydrazone of  $\alpha$ -naphthalenesulphonylformyl cyanide, orange-red leaflets, m. p. 193° [potassium salt, golden-yellow, shining crystals (+ 3H<sub>2</sub>O); silver salt, dark yellow, amorphous precipitate; sodium salt, freely soluble in water];  $\alpha$ -naphthalenesulphonyl-o-tolueneazoacetonitrile or o-tolylhydrazone of  $\alpha$ -naphthalenesulphonylformyl cyanide, dark yellow, prismatic needles, m. p. 149—150° (potassium salt, pale yellow needles; sodium salt, freely soluble in water);  $\alpha$ -naphthalenesulphonyl-p-anisoleazoacetonitrile or p-methoxyphenylhydrazone of  $\alpha$ -naphthalenesulphonylformyl cyanide, carmine-red, prismatic needles, m. p. 173° [potassium salt, pale yellow, six-sided crystals (+ H<sub>2</sub>O); sodium salt, freely soluble in water];  $\beta$ -naphthalenesulphonylbenzeneazoacetonitrile or phenylhydrazone of  $\beta$ -naphthalenesulphonylformyl cyanide, red needles, m. p. 194—195° [potassium salt (+ 3H<sub>2</sub>O), yellowish-brown, shining crystals; sodium salt, freely soluble in water; lead salt, lemon-yellow,

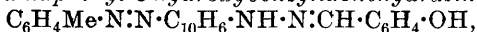
amorphous precipitate];  $\beta$ -naphthalenesulphonylacetonitrile has m. p.  $109^\circ$  (instead of  $95^\circ$ , as previously given); methylation of the substance, m. p.  $194$ — $195^\circ$ , by methyl iodide and sodium ethoxide at  $100^\circ$  gives a product, yellowish-red crystals, m. p.  $168^\circ$ , which differs from the corresponding propionyl compound (see later), but other analogous experiments failed to give so definite a result;  $\beta$ -naphthalenesulphonyl-p-tolueneazoacetoneitrile or p-tolylhydrazone of  $\beta$ -naphthalenesulphonylformyl cyanide, orange-coloured needles, m. p.  $189$ — $190^\circ$  [potassium salt ( $+0.5\text{H}_2\text{O}$ ), amorphous, egg-yellow substance; sodium salt, freely soluble in water; silver salt, amorphous, dark yellow precipitate]; methylated product, pale yellow needles, m. p.  $210$ — $211^\circ$ ;  $\beta$ -naphthalenesulphonyl-m-tolueneazoacetoneitrile or m-tolylhydrazone of  $\beta$ -naphthalenesulphonylformyl cyanide, red, prismatic needles, m. p.  $160$ — $161^\circ$  (potassium salt, reddish-yellow crystals; sodium salt, freely soluble in water);  $\beta$ -naphthalenesulphonyl-p-phenetoleazoacetoneitrile or p-ethoxyphenylhydrazone of  $\beta$ -naphthalenesulphonylformyl cyanide, pale brown crystals, m. p.  $165$ — $166^\circ$  [potassium salt ( $+3\text{H}_2\text{O}$ ), dark yellow, hexagonal crystals]; p-bromobenzenesulphonylbenzeneazoacetoneitrile or phenylhydrazone of p-bromobenzenesulphonylformyl cyanide, yellowish-brown prisms, m. p.  $185^\circ$  (sodium salt, pale yellow, amorphous precipitate); p-bromobenzenesulphonyl-p-phenetoleazoacetoneitrile or p-ethoxyphenylhydrazone of p-bromobenzenesulphonylformyl cyanide, pale brown, prismatic needles, m. p.  $154$ — $155^\circ$  (sodium salt, dark yellow crystals) (in the two cases last mentioned, the salts can only be prepared in the absence of moisture); benzenesulphonylbenzeneazopropionitrile,  $\text{SO}_2\text{Ph}\cdot\text{CMe}(\text{N}_2\text{Ph})\cdot\text{CN}$ , canary-yellow, prismatic needles, m. p.  $78^\circ$ ; benzenesulphonyl-p-tolueneazopropionitrile, red, prismatic needles, m. p.  $103$ — $104^\circ$ ; benzenesulphonyl-p-anisoleazopropionitrile, lemon-yellow needles, m. p.  $81$ — $82^\circ$ ; benzenesulphonyl-p-phenetoleazopropionitrile, pale yellow crystals, m. p.  $96$ — $97^\circ$ ;  $\beta$ -naphthalenesulphonylpropionitrile, colourless, waxy crystals, m. p.  $90$ — $91^\circ$ ;  $\beta$ -naphthalenesulphonylbenzeneazopropionitrile, dark yellow tetrahedra, m. p.  $120^\circ$ ;  $\beta$ -naphthalenesulphonyl-p-tolueneazopropionitrile, dark yellow prisms, m. p.  $119$ — $120^\circ$ ; p-chlorobenzenesulphonylbenzeneazopropionitrile, dark yellow rhombs, m. p.  $90$ — $91^\circ$ ; p-chlorobenzenesulphonyl- $\beta$ -naphthaleneazopropionitrile, pale yellow, silky needles, m. p.  $154$ — $155^\circ$ ; p-bromobenzenesulphonyl-p-tolueneazopropionitrile, dark yellow, prismatic needles, m. p.  $151^\circ$ ; p-bromobenzenesulphonyl-p-anisoleazopropionitrile, sulphur-yellow prisms, m. p.  $153^\circ$ .

H. W.

*o*-, *m*-, and *p*-Tolueneazo- $\alpha$ -naphthylhydrazinesulphonic Acids. J. TRÖGER and G. LANGE (*J. pr. Chem.*, 1920, [ii], 101, 123—135. Compare A., 1906, i, 120; 1909, i, 68, 69; 1910, i, 207).—The *o*-, *m*-, and *p*-tolueneazo- $\alpha$ -naphthylamines are diazotised, and the resulting solutions are filtered into alkaline potassium sulphite solution, thus yielding the potassium diazo-

sulphonates,  $C_6H_4Me \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot SO_3K$ ; the latter are reduced by ammonium sulphide to the corresponding potassium hydrazine sulphonates,  $C_6H_4Me \cdot N_2 \cdot C_{10}H_6 \cdot NH \cdot NH \cdot SO_3K$  (which are somewhat readily decomposed), from which the free sulphonic acids are readily isolated. The yields are dependent on the smoothness with which the primary material can be diazotised; with the ortho- and meta-derivatives, this occurs readily at  $0^\circ$ , but with the para-compound it is best effected at  $20^\circ$ , the process, however, being rather unsatisfactory even in this case. The hydrazinesulphonic acid reacts with aromatic aldehydes to yield hydrazones; heating during the reaction must not be prolonged, and the meta- and para-compounds are more sensitive than the ortho-derivatives.

The following substances are described: *potassium p-tolueneazo- $\alpha$ -naphthylldiazosulphonate* (labile salt, amorphous, reddish-brown flocks; stable salt, dark brown powder); *potassium p-tolueneazo- $\alpha$ -naphthylhydrazinesulphonate*, pale brown needles; *p-tolueneazo- $\alpha$ -naphthylhydrazinesulphonic acid*, blackish-violet crystals; *p-tolueneazo- $\alpha$ -naphthyl-o-hydroxybenzylidenehydrazine*,



dark reddish-brown, prismatic needles, m. p.  $166 \cdot 5^\circ$  (*hydrochloride*, dark moss-green, crystalline powder); *p-tolueneazo- $\alpha$ -naphthylcinnamylidenehydrazine*, dark reddish-brown, prismatic crystals, m. p.  $168 \cdot 5^\circ$  after previous softening (*hydrochloride*, black powder with green glance); *p-tolueneazo- $\alpha$ -naphthylanisylidenehydrazine*, small, brown, shining crystals, m. p.  $156^\circ$  (*hydrochloride*, blackish-green crystals); *tolueneazo- $\alpha$ -naphthyl-p-tolylidenehydrazine*, blackish-brown, oblique crystals, m. p.  $159^\circ$  (*hydrochloride*, small, bluish-black crystals).

*o-Tolueneazo- $\alpha$ -naphthylamine*, pale red, silky needles, m. p.  $99^\circ$  [the *hydrochloride*, violet needles, *sulphate*, pale violet crystals ( $+3H_2O$ ), and the *nitrate*, blackish-green crystals, are described], is most conveniently prepared by the addition of diazotised *o*-toluidine solution to an alcoholic solution of  $\alpha$ -naphthylamine at  $45^\circ$ . It gives rise to the following compounds: *potassium o-tolueneazo- $\alpha$ -naphthylldiazosulphonate* (red, labile, and rust-red stable salt); *potassium o-tolueneazo- $\alpha$ -naphthylhydrazinesulphonate*, pale brown, silky leaflets; *o-tolueneazo- $\alpha$ -naphthylhydrazinesulphonic acid*, amorphous, violet-black flocks; *o-tolueneazo- $\alpha$ -naphthyl-o-hydroxybenzylidenehydrazine*, coarse, dark brown crystals, m. p.  $162^\circ$  (*hydrochloride*, bluish-green, crystalline powder); *o-tolueneazo- $\alpha$ -naphthylcinnamylidenehydrazine*, brown prisms, m. p.  $170^\circ$  (*hydrochloride*, coarse, black, crystalline powder); *o-tolueneazo- $\alpha$ -naphthylanisylidenehydrazine*, brown, shining leaflets, m. p.  $153^\circ$  (*hydrochloride*, small, dark blue crystals); *o-tolueneazo- $\alpha$ -naphthyl-p-tolylidenehydrazine*, coffee-brown crystals, m. p.  $152^\circ$  (*hydrochloride*, black, shining, crystalline powder).

*m-Tolueneazo- $\alpha$ -naphthylamine*, blood-red crystals, m. p.  $107^\circ$  [*nitrate*, bluish-violet needles; *chloride* ( $+2H_2O$ ), black, silky needles; *sulphate*, steel-blue rods], yields *potassium m-tolueneazo-*

*α-naphthylhydrazinesulphonate*, small, reddish-brown needles, and *m-tolueneazo-α-naphthylhydrazinesulphonic acid*, violet crystals. The latter reacts with anisaldehyde to give *m-tolueneazo-α-naphthylanisylidenehydrazine*, small, coffee-brown crystals, m. p. 159—160° (*hydrochloride*, bluish-black, crystalline powder).

H. W.

*o-* and *p*-**Tolueneazoglyoxalines**. FRANK LEE PYMAN and LEONARD ALLAN RAVALD (*T.*, 1920, **117**, 1426—1429).

**Nitro-derivatives and Nitrohydrazones. II.** R. CIUSA and L. VECCHIOTTI (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 42—47. Compare *A.*, 1912, i, 133; this vol., i, 256).—The tendency of the phenylhydrazones of aromatic nitro-aldehydes to furnish chromo-isomerides is exhibited to an enhanced degree by the nitrophenylhydrazones. As regards the cause of this isomerism, it has been found previously (*A.*, 1912, i, 33) that, whereas benzaldehydephenylhydrazone (1 mol.) forms an additive compound with 2 mols. of picryl chloride, each of the phenylhydrazones of the three nitrobenzaldehydes unites with only 1 mol. of the chloride, although benzaldehydenitrophenylhydrazone unites with 2 mols. The conclusion is drawn that the points of attack in the molecules of trinitrobenzene and its derivatives are the phenyl group of the aldehyde and the iminic nitrogen atom. In order to test this conclusion, additive compounds of benzaldehydephenylhydrazone with two different trinitrobenzene derivatives have been prepared with the hope of obtaining two such isomerides as

$C_6H_2Cl(NO_2)_3 \cdots \cdots CHPh:N:NHPh \cdots \cdots C_6H_2Me(NO_2)_3$   
and  $C_6H_2Me(NO_2)_3 \cdots \cdots CHPh:N:NHPh \cdots \cdots C_6H_2Cl(NO_2)_3$ ; as yet, no such isomerides have been obtained.

The possibility that, in the chromo-isomeric nitrophenylhydrazones, the nitro-group is united internally by secondary valencies either to the iminic nitrogen atom or to the phenyl group of the aldehyde, is also discussed.

The experimental results obtained are to be published separately.

T. H. P.

**The Influence of Reaction on the Precipitation of Protein by Tannin.** TORALD SOLLMANN (*J. Pharm. expt. Ther.*, 1920, **16**, 49—59).—The precipitation of proteins by tannin depends on the hydrogen-ion concentration of the medium. The application of these observations to the clinical use of astringents is discussed.

J. C. D.

**The Balloelectricity of Amphoteric Substances.** C. CHRISTIANSEN and JOHANNE CHRISTIANSEN (*Zeitsch. physiol. Chem.*, 1919, **107**, 7—28).—The isoelectric point of certain substances, such as albumin, leucine, etc., is identical with the isoballoelectric point. Other ampholytes, such as glycine, alanine, etc., show no isoballoelectric point. The authors presume that



this differentiation in balloelectric behaviour of ampholyte ions is connected with the hydration of the ions. S. S. Z.

**Ion Series and the Physical Properties of Proteins. I.** JACQUES LOEB (*J. Gen. Physiol.*, 1920, **3**, 85—105).—Experiments are described on the influence of acids and alkalis on the osmotic pressure of solutions of crystalline egg-albumin and of gelatin, and on the viscosity of solutions of gelatin. It was found that in all cases there was no difference in the effects of hydrochloric, hydrobromic, nitric, acetic, mono-, di-, and tri-chloroacetic, succinic, tartaric, citric, and phosphoric acids on these physical properties when the solutions of the protein with these different acids have the same hydrogen-ion concentration and the same concentration of originally isoelectric protein. It was possible to show that in all the protein acid salts named, the anion in combination with the protein is univalent.

The strong bibasic sulphuric acid forms protein acid salts with a bivalent anion,  $\text{SO}_4$ , and the solutions of protein sulphate have an osmotic pressure and a viscosity of only half or less than that of a protein chloride solution of the same concentration of hydrogen ions and originally isoelectric protein. Oxalic acid behaves essentially like a weak bibasic acid, although it seems that a small part of the acid combines with the protein in the form of bivalent anions. It was found that the osmotic pressure and viscosity of solutions of lithium, sodium, potassium, and ammonium salts of a protein are the same at the same hydrogen-ion concentration and the same concentration of originally isoelectric protein. Calcium and barium hydroxides form salts in which the cation is bivalent, and the osmotic pressures and viscosity of solutions of these two metal proteinates are only one-half or less than half of that of sodium proteinate of the same concentrations of hydrogen ion and originally isoelectric protein.

These results exclude the possibility of expressing the effect of acids and alkalis on the osmotic pressure of solutions of gelatin and egg-albumin, and on the viscosity of solutions of gelatin in the form of ion series. The different results of former workers were probably chiefly due to the fact that the effects of acids and alkalis on these proteins were compared for the same quantity of acid and alkali instead of for the same  $p_{\text{H}}$ . J. C. D.

**A Tripeptide from Casein which contains Tryptophan.** SIGMUND FRÄNKEL and ERNST NASSAU (*Biochem. Zeitsch.*, 1920, **110**, 287—298).—The tripeptide was prepared in the following way. Casein was digested with potassium hydroxide, and, when hydrolysis was complete, the solution was neutralised and acidified with sulphuric acid. A precipitate was formed. The filtrate was treated with 10% sulphuric acid and 10% mercuric sulphate, and the precipitate thus obtained decomposed with hydrogen sulphide in the presence of barium carbonate. It was then purified by various treatments with ethyl and methyl alcohol, and finally precipitated as the barium salt from methyl alcohol with ether. Analysis gave the formula  $\text{C}_{50}\text{H}_{76}\text{O}_{20}\text{N}_{10}\text{Ba}$ ; decomp. 175—195°.

It was shown to contain  $12\text{H}_2\text{O}$ . The estimation of tryptophan in the barium compound showed that the tripeptide contained 2 molecules of it. It was also shown to contain one amino-group by Van Slyke's method. The tripeptide gave a very weak biuret reaction. On hydrolysing it with hydrochloric acid and on benzoylating it, *dl*-benzoylalanine, m. p.  $163^\circ$ , was obtained. The tripeptide has the formula  $\text{C}_{25}\text{H}_{27}\text{O}_4\text{N}_5$ , and is to be regarded as derived from 2 molecules of tryptophan and 1 molecule of alanine, with elimination of  $2\text{H}_2\text{O}$ . S. S. Z.

**Preparation of Compounds of Nucleic Acid and Yohimbine which Dissolve Readily to Clear Solutions.** ERNST WEINERT (D.R.-P. 322996; from *Chem. Zentr.*, 1920, iv, 451).—Nucleic acid and yohimbe bases are mixed in the presence of ammonia, or ammonium nucleate is treated with salts of yohimbine or the total base of the yohimbe bark. *Yohimbine nucleate*,  $\text{C}_{20}\text{H}_{30}\text{O}_4\text{N}_2\cdot\text{C}_{40}\text{H}_{53}\text{O}_{26}\text{N}_{14}\text{P}_4$ , is a yellowish- or greenish-white, amorphous powder, which has a feebly acidic taste and almost neutral reaction; it is readily soluble in water, and is expected to find therapeutic application. H. W.

**Nuclein Metabolism. VII. Isolation of Crystalline Adenosinephosphoric Acid.** S. J. THANNHAUSER (*Zeitsch. physiol. Chem.*, 1919, 107, 157—164. Compare A., 1918, i, 316).—A mononucleotide, adenosinephosphoric acid, was obtained in the following way. The brucine salt of a triphosphonucleic acid (A., 1918, i, 47) was decomposed with ammonia, and the mixture of ammonium salts was further treated with lead acetate. The lead salts were then decomposed with hydrogen sulphide and the solution concentrated in a vacuum. After twenty-four hours, fine, colourless needles separated of adenosinephosphoric acid, m. p.  $208^\circ$  (decomp.),  $[\alpha]_D^{20} - 48.03^\circ$ . The brucine salt has m. p.  $180$ — $182^\circ$ . The nucleotide was hydrolysed with ammonia in the autoclave, and adenosinephosphoric acid, as well as the unchanged nucleotide, was obtained. S. S. Z.

**The Swelling of Gelatin in Acids.** W. R. ATKIN (*J. Soc. Leather Tr. Chem.*, 1920, 4, 248).—The quantity  $e$  (see T., 1916, 109, 307) and the swelling of gelatin by solutions of various monobasic acids are functions of the hydrion concentration of the external acid solution, attain a maximum at  $P_{\text{H}}=2.4$ , and minimum at  $P_{\text{H}}=4.6$ , the isoelectric point of gelatin. D. W.

**Production of a Contracting Clot in a Gel of Gelatin at the Isoelectric Point.** DOROTHY JORDAN LLOYD (*Biochem. J.*, 1920, 14, 584—585).—A sample of highly purified gelatin, prepared by a slight modification of the method of Dheré and Gorgolewski (A., 1910, i, 448), was dissolved in distilled water by heating, and cooled to  $18^\circ$ . The reaction of the solution at this temperature was  $P_{\text{H}}=6.09$ . The gel which formed showed visible contraction after twenty-four hours. The experiments demonstrate that gelatin gels are unstable at the isoelectric point. Small quantities of sodium hydroxide have the same stabilising influence

as small quantities of hydrochloric acid. The formation of stable gels, therefore, is only possible in the presence of electrolytes.

J. C. D.

**The Free Amino-groups of the Proteins. I.** S. EDLBACHER (*Zeitsch. physiol. Chem.*, 1919, **107**, 52—72).—The *N*-methyl values of proteins of different origin and composition, such as gelatin, casein, globin, Bence-Jones protein, edestin, and pumpkin globulin, are of the same order. Clupeine sulphate and sturine sulphate also show similar *N*-methyl values, whilst esocine sulphate and scombrine sulphate are not methylated at all. Gelatin hydrolysed with alkali hydroxide for half an hour gives a higher *N*-methyl value than unhydrolysed gelatin. On hydrolysing gelatin with acid, the ratio *N*-methyl value/"formol" value falls after the first half an hour of hydrolysis to about a half of the original value, but remains constant after that. The same fall in the ratio of the two values is observed when gelatin and casein and clupeine sulphate are hydrolysed by tryptic digestion.

S. S. Z.

**The Preparation of Highly Active Saccharase (Invertase) Preparations.** HANS EULER and OLOF SVANBERG (*Zeitsch. physiol. Chem.*, 1919, **107**, 269—313).—Various highly potent preparations of saccharase were obtained from autolysed yeast by means of precipitation with alcohol. The potency of the different preparations was estimated quantitatively. It was found that about two-thirds of the total saccharase of the autolysed yeast remains in the pasty part after the juice has been filtered off. The authors calculate from the relative activities of one of their purest preparations and of dried yeast that their preparation of saccharase forms about 1/100th part by weight of the total dry matter of the cell. Allowing for the moisture of the fresh yeast cell and for the saccharase retained by the pasty portion of the autolysed yeast, their active preparation would therefore form 1/900th part of the fresh yeast from which it was prepared. The authors at the same time admit that their best preparation is by no means pure.

S. S. Z.

**The Theory of Invertase Action.** L. MICHAELIS and M. ROTHSTEIN (*Biochem. Zeitsch.*, 1920, **110**, 217—233).—Invertase combines with one molecule of sucrose, and forms an acid having the dissociation constant  $3 \times 10^{-7}$ . The undissociated molecules of this acid decompose spontaneously into the products of the enzymic degradation. The anions, on the other hand, are stable. The theory explains the influence of the reaction on the action of the enzyme within certain limits of hydrogen-ion concentration.

S. S. Z.

**Resistance of Emulsin Enzymes to the Prolonged Action of 70% Methyl Alcohol.** MARC BRIDEL (*J. Pharm. Chim.*, 1920, [vii], **22**, 323—327).—When emulsin is kept in contact with 70% methyl alcohol for five years, the activity of the enzymes present is diminished, but not destroyed: the enzymes which act on lactose

and  $\beta$ -ethylgalactoside appear to be more resistant than the  $\beta$ -glucosidase.

W. P. S.

**Investigations on the Influence of Temperature on Enzymes, especially on Rennet and Pepsin.** ADOLF KÖNIG (*Biochem. Zeitsch.*, 1920, **110**, 266—286).—Rennet and thrombin are more stable at high temperatures in concentrated solutions and in glycerol than in dilute solutions. The inactivation of rennet by heat may be delayed by increasing the quantity of milk, as it contains protective substances. The increase in temperature up to a certain limit accelerates the action of rennet. The inactivating influence becomes evident only at 45°. The inactivation of pepsin and diastase also only becomes apparent at 45°. No difference as regards its behaviour to heat is observed in concentrated and in dilute solutions of pepsin. The different behaviour of pepsin and rennet as regards heat supports the theory that they are different enzymes.

S. S. Z.

**Triphenylarsine and Diphenylarsenious Salts.** WILLIAM JACKSON POPE and EUSTACE EBENEZER TURNER (*T.*, 1920, **117**, 1447—1452).

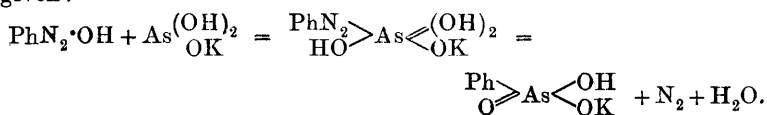
**A New Type of Compound containing Arsinic.** GEORGE JOSEPH BURROWS and EUSTACE EBENEZER TURNER (*T.*, 1920, **117**, 1373—1383).

**The Theory of Electrolytic Ions. XVIII. Mobility and Space-filling of Arsinic Acid Ions.** RICHARD LORENZ and ERIKA SCHMIDT (*Zeitsch. anorg. Chem.*, 1920, **112**, 269—277).—The conductivities of the sodium salts of a number of substituted phenylarsinic acids (compare this vol., i, 777) have been used to calculate the ionic mobilities of the corresponding anions. The upper and lower limits of the ionic mobilities were also calculated from the "space-filling numbers," and in every case the mobility calculated from the conductivity was below the lower limit calculated from the space-filling number (compare this vol., ii, 481). The densities of the free acids were determined at 20°, and the following values are given: arsanilic, 1.9571; *o*-aminotolylarsinic, 1.7475; *o*-diaminophenylarsinic, 1.8313; dimethylaminophenylarsinic, 1.6746; *m*-dihydroxyphenylarsinic, 2.0040; 3-nitro-4-aminophenylarsinic, 2.0359; dichlorohydroxyphenylarsinic, 2.1029; dibromohydroxyphenylarsinic, 2.4150; 3-nitro-4-hydroxyphenylarsinic, 2.0314; *p*-phenylenediarsinic, 2.2025; dinitrohydroxyarsinic, 2.0565. Kopp's law was applied to calculate the atomic volume of arsenic in these compounds, but results ranging from 11.2 to 33.3 were obtained from different compounds. E. H. R.

**The Diazo-synthesis of Aromatic Arsinic Acids and its Theoretical Significance in Connexion with similar Actions. A By-product containing Arsenic.** HANS SCHMIDT (*Annalen*, 1920, **421**, 159—174).—The spontaneous and immediate evolution of nitrogen and the formation of sodium arsenate during the action of diazonium solutions on sodium arsenite have been investigated by Königs and Guttman (A., 1912, i, 397), whilst

subsequently the author and Bart have independently observed that the arsenic radicle becomes attached to the nucleus in place of the diazo-groups (D.R.-P. 250264 and 264924). It is now shown that the most favourable conditions for the production of phenylarsinic acid from a benzenediazonium salt and many of the nucleus-substituted derivatives are secured when the alkalinity of the solution is so regulated that reaction can occur in accordance with the scheme:  $\text{PhN}_2\text{Cl} + \text{AsO}_3\text{HK}_2 = \text{AsPhO}_3\text{HK} + \text{KCl} + \text{N}_2$ . The process then occurs spontaneously, and the diazo-compound is rapidly destroyed. In this manner, *o*-nitrobenzenediazonium chloride gives about 90% of the theoretical quantity of *o*-nitrophenylarsinic acid, but the amounts of arsenic-free by-products (azo-compounds, etc.) are more considerable in the cases of many other arsenic acids. In more strongly alkaline solution, the reducing action is more generally noticeable, and the yields of arsenic acids are lower. Poorer yields are also observed with a benzenediazonium salt in acid solution, but an acid medium is favourable when strongly acidic substituents are present in the benzene nucleus.

The theoretical interpretation of the reaction, in which the arsenic passes from the trivalent to the quinquivalent condition, offers considerable difficulties, but may be generally considered in conjunction with a number of other actions (formation of nitro-derivatives and sulphonic acids from diazo-compounds and nitrous or sulphurous acids and of alkyl-sulphonic, phosphinic, arsenic acids, etc., from alkyl haloids, and the salts of sulphurous, phosphorous, and arsenious acids, etc.) which have the common feature that an element passes from a lower to a higher valency by intramolecular atomic displacement and without the aid of an oxidising agent. The case of arsenious acid has been met, to some extent, by considering it to react in the form  $\text{O}:\text{AsH}(\text{OH})_2$  instead of  $\text{As}(\text{OH})_3$ , but, in the author's opinion, a more general conception is obtained by adopting the following hypothesis. The acids  $\text{H}_2\text{SnO}_2$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{HNO}_2$ ,  $[\text{H}_3\text{PO}_3]$ ,  $\text{H}_3\text{AsO}_3$ , and  $\text{H}_3\text{SbO}_3$  can exist in modifications which contain one hydrogen atom in a peculiar form, and this labile variety becomes stabilised when the hydrogen atom is replaced by an organic radicle. Such replacement occurs when the salts of  $\text{H}_2\text{SnO}_2$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{HNO}_2$ ,  $(\text{H}_3\text{PO}_3)$ , and  $\text{H}_3\text{AsO}_3$  are treated with organic haloids, or when  $\text{H}_2\text{SO}_3$ ,  $\text{HNO}_2$ ,  $\text{H}_3\text{AsO}_3$ , or  $\text{H}_3\text{SbO}_3$ , as acids or salts, react with diazonium compounds, with evolution of nitrogen. The acids mentioned above yield additive compounds with alkyl haloids or diazo-compounds in the same manner as with oxygen, which, by elimination of alkali haloid or water and nitrogen, pass into derivatives of saturated acids with central atoms exhibiting higher valency. For the particular case under more immediate consideration, the following scheme is given:



In addition to the well-known arsenic-free by-products (such as benzene, azobenzene, hydrazobenzene, and aniline), others containing arsenic can also be isolated, the chief of which is diphenyl-4-arsinic acid,  $C_6H_4Ph \cdot AsO_3H_2$ ; since this substance is not obtained from benzenediazonium chloride and phenylarsinic acid, it must be assumed that a hydrogen atom of the benzene nucleus becomes labile at the moment at which the replacement of the diazo-residue by the arsenic group takes place, an explanation of the phenomenon being possibly found in Cain's method (T., 1907, **91**, 1049) of formulating diazo-compounds.

The preparation of the following individual compounds is described in detail: phenylarsinic acid, m. p.  $156^\circ$ ; *phenyl-p-phenylene*arsinic [*diphenyl-4-arsinic*] acid, m. p. not below  $300^\circ$ , corresponding chloride, m. p.  $78-80^\circ$  [Lettermann (*Inaug. Diss.*, Rostock, 1911) gives m. p.  $275^\circ$  and  $74^\circ$  respectively]; *o-nitrophenylarsinic acid*, yellow needles, m. p. about  $232^\circ$  (decomp.) when rapidly heated, obtained in 86% yield (the *magnesium* salt, woolly needles, is described); *m-nitrophenylarsinic acid*, shining leaflets, which pass into the anhydride at a temperature which entirely depends on the manner of heating; 2:3'-*dinitrodiphenyl-4-arsinic acid*,  $NO_2 \cdot C_6H_4 \cdot C_6H_3(NO_2) \cdot AsO_3H_2$ , pale brown powder, which slowly darkens above  $230^\circ$ , but is not molten at  $260^\circ$ ; *p-acetylaminophenylarsinic acid*; *p-aminophenylarsinic acid*.

H. W.

**Quantitative Studies in Chemotherapy. III. The Oxidation of Arsphenamine [Salvarsan].** CARL VOEGTLIN and HOMER W. SMITH (*J. Pharm. exp. Ther.*, 1920, **16**, 199—217. Compare this vol., i, 792).—The sodium salts of arsenious acid, methyl and ethyl arsenious oxide, phenyl- and diphenyl-arsenious oxide, and *p*-aminophenylarsenious oxide are relatively very stable towards atmospheric oxygen. Salvarsan [3:3'-diamino-4:4'-dihydroxyarsenobenzene] dihydrochloride, contrary to the prevalent views, is exceedingly stable towards atmospheric oxygen. The addition of alkali leads to a rapid increase in the rate of oxidation. The sodium salt of salvarsan is oxidised first to the corresponding oxide, and then to the quinquivalent compound. *m*-Amino-*p*-hydroxyphenylarsenious oxide ("arsenoxide") is oxidised only in alkaline solution. The nature of the process curve indicates that the reaction is catalysed by a reaction product.

Neosarsphenamine [neosalvarsan] shows rapid oxidation on exposure to air.

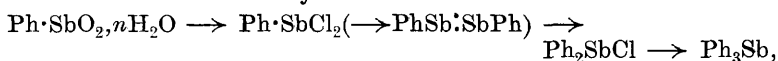
The nature and rate of oxidation of salvarsan and neosalvarsan to the corresponding oxides furnish an explanation of the increase in toxicity and trypanocidal activity of these compounds when their solutions are exposed to air.

J. C. D.

**The Colloidal Properties of Aqueous Solutions of "Salvarsan."** Z. KLEMENSIEWICZ (*Bull. Soc. chim.*, 1920, [iv], **27**, 820—824).—The viscosity of aqueous solutions of salvarsan

increases from the moment of preparation, ultimately reaching an approximately constant value much higher than the initial value. The initial velocity of increase of the viscosity, as well as the final value of the viscosity, increase very considerably with the concentration of the solution. If a 10% solution, the viscosity of which has reached its final value, is diluted to 4%, a solution is obtained the viscosity of which is higher than the final viscosity of a 4% solution prepared directly from salvarsan. The viscosity of the diluted solution diminishes, however, on keeping to its correct value. Rise in temperature increases the rate at which a solution attains its final viscosity, but diminishes the value of the latter. The presence of acid or alkali has a marked effect on the viscosity of salvarsan solutions. W. G.

**The Diazo-synthesis of Aromatic Stibinic Acids and the Investigation of their Polymeric Constitution. Aromatic Derivatives of Antimony Pentachloride and its Additive Compounds.** HANS SCHMIDT (*Annalen*, 1920, **421**, 174—246. Compare Hasenbäumer, A., 1899, i, 209; Michaelis and Günther, A., 1911, i, 1056; Morgan and Micklethwait, T., 1911, **99**, 2286; May, T., 1912, **101**, 1033; Grüttner and Wiernik, A., 1916, i, 96, 98).—Arylstibinic acids are readily prepared by the action of diazo-compounds on antimonious acid and its salts. In contrast to the similar reaction with arsenious acid, the method may even be applied in concentrated alkaline solution, although when strongly acidic substituents are present in the nucleus, it is frequently preferable to operate in neutral or acid solution. The arylstibinic acids are shown, in general, to be derived from polymerised antimonious acids, and to be pronouncedly colloidal in their properties. The reactions indicated by the scheme



have been realised, whereas previously they have only been accomplished with difficulty in the reverse direction.

Phenylstibinic acid is prepared by the gradual addition of a solution of antimony oxide in hydrochloric acid to benzenediazonium chloride, and subsequent treatment with an excess of sodium hydroxide solution, when copious evolution of nitrogen immediately occurs; alternatively, May's additive compound of benzenediazonium chloride and antimony trichloride is treated with an excess of cold dilute sodium hydroxide solution, whereupon nitrogen is gradually evolved. The crude product is best purified by conversion into the double salt of phenylstibine tetrachloride and ammonium chloride (see later), which is subsequently decomposed by water. Analyses of phenylstibinic acid give results in agreement with the formulae  $(3\text{Ph} \cdot \text{SbO}_2, n\text{H}_2\text{O})$  and  $(3\text{Ph} \cdot \text{SbO}_2, 2\text{H}_2\text{O})$ ,

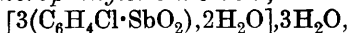
but more information with regard to its constitution is derived from a study of its behaviour towards alkali. It is found that considerably less than one molecular proportion of alkali is required

to effect the solution of phenylstibinic acid, and that a solution prepared in this manner gradually becomes increasingly acid until a final point is reached. The phenomenon is caused by polymerisation and depolymerisation. The precipitated isolated phenylstibinic acid is a polymeric form, which is slowly decomposed to the unimolecular form in solution in the presence of alkali; the latter is only stable in the form of its alkali salts, and, when liberated, becomes again polymerised. Initial neutralisation occurs when the ratio Na:Sb is approximately 1:3, thus pointing to a trimolecular formula, probably



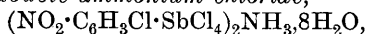
but possibly admixed with  $\text{OH}\cdot\text{SbOPh}\cdot\text{O}\cdot\text{SbPh}(\text{OH})_2\cdot\text{O}\cdot\text{SbOPh}\cdot\text{OH}$ ; the final neutralisation value is somewhat less than that calculated for complete conversion into the unimolecular form, but this observation rests on the assumption that the colour change occurs with phenolphthalein when sodium hydroxide and the stibinic acid are mixed in molecular proportions. Phenylstibinic acid unites with hydrogen sulphide to yield pale yellow sulphides, which are decomposed when warmed, with partial formation of antimony sulphide. *Phenylstibine tetrachloride*,  $\text{PbSbCl}_4$ , is obtained when phenylstibinic acid is treated with concentrated hydrochloric acid and the solution evaporated at a moderate temperature; the freshly prepared substance has m. p.  $60-65^\circ$ , which rises to about  $100^\circ$  when it is preserved for some weeks in a vacuum, but partial decomposition takes place simultaneously. When heated, it dissociates into chlorine and dichlorophenylstibine, and the latter is further decomposed into chlorodiphenylstibine and antimony chloride. Its solution in concentrated hydrochloric acid unites with ammonium chloride, giving  $\text{SbCl}_5\text{PhNH}_4$ , pale yellow, voluminous powder, which does not change below  $260^\circ$ , and similar salts are formed with the hydrochlorides of aniline, dimethylaniline, pyridine, quinoline, dicyandiamidine, guanidine, carbamide, ethylaniline, and allylamine; methyl- and ethylamines behave somewhat differently, yielding precipitates, which are initially white, but rapidly become yellow.

*m*-Nitrophenylstibinic acid,  $[\text{3}(\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SbO}_2), 2\text{H}_2\text{O}], 3\text{H}_2\text{O}$  (compare Morgan and Micklethwait, *loc. cit.*), is prepared by the nitration of phenylstibinic acid by nitric acid (D 1.515), or by nitric and sulphuric acids at the ordinary temperature; it is more rapidly depolymerised by alkali than the parent acid. The corresponding *chloride*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SbCl}_4\cdot\text{H}_2\text{O}$ , m. p.  $140^\circ$  (decomp.), and *double ammonium chloride*, colourless crystals ( $+ \frac{1}{3}\text{H}_2\text{O}$ ), which soften above  $235^\circ$ , are described. The acid is also obtained, but less advantageously, by the action of *m*-nitrobenzenediazonium chloride on potassium antimonyl tartrate in faintly acid solution. *o*-Nitrophenylstibinic acid forms a pale yellowish-brown powder, which remains unchanged below  $285^\circ$ , and with alcoholic hydrogen chloride gives the corresponding *chloride*, crystalline leaflets, m. p. about  $127^\circ$ . *p*-Chlorophenylstibinic acid,





closely resembles phenylstibinic acid; it is converted by hydrochloric acid into an unstable, yellow chloride, which gives the corresponding *double ammonium chloride*, lemon-yellow precipitate, which remains unchanged below  $250^{\circ}$ . *p*-Chloro-*m*-nitrophenylstibinic acid forms an almost colourless powder, which is unaltered below  $285^{\circ}$ ; the *chloride*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{SbCl}_4 \cdot 5\text{H}_2\text{O}$ , has m. p. about  $80^{\circ}$  after previous softening, whilst the *monohydrate* softens at about  $122^{\circ}$ ; the *double ammonium chloride*,

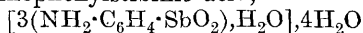


forms a colourless, voluminous precipitate, m. p. above  $220^{\circ}$  (decomp.) after previous softening. With the acids in general, it is found that the presence of acid substituents causes a marked acceleration of the process of hydration, whilst the basic amino-group effects a distinct retardation. *m*-Nitro-*p*-hydroxyphenylstibinic acid,  $[\text{3}(\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{SbO}_2) \cdot 2\text{H}_2\text{O}] \cdot 5\text{H}_2\text{O}$ , prepared by the action of concentrated aqueous potassium hydroxide on the corresponding chloro-acid, is a yellowish-brown powder, which gradually darkens above  $230^{\circ}$ ; the corresponding *chloride* and *double ammonium chloride* are stable substances. *p*-Anisylstibinic acid gives a remarkably unstable chloride.

The possibility of preparing the phenylstibinic acids readily and in good yield has rendered the isolation of the antimonylaryls a comparatively easy matter, and many of them are described. In general, they are amorphous substances, in which the acidic properties of antimony oxide are no longer manifest; with halogen acids, on the other hand, they form characteristic compounds,  $\text{ArSbHal}_2$ , in which the halogen is either not hydrolytically removed or is replaced with greater difficulty than in antimony chloride. When heated alone or in certain solvents, they tend to decompose, according to the scheme  $\text{Ph} \cdot \text{SbO} \rightarrow (\text{Ph}_2\text{Sb})_2\text{O} \rightarrow \text{Ph}_3\text{Sb}$ , the action being both positively and negatively catalysed by a number of reagents in an apparently irregular manner. The physiological action of derivatives of tervalent differ markedly from those of quinquevalent antimony, since the former vigorously attack the skin and mucous membrane. Phenylstibine oxide,  $\text{SbPhO}$ , voluminous powder, which softens at  $153$ – $154^{\circ}$  (Hasenbäumer, *loc. cit.*, gives m. p.  $150^{\circ}$ ), is prepared by the action of sulphur dioxide in the presence of a little sodium iodide on an ice-cold aqueous methyl-alcoholic solution of phenylstibinic acid and concentrated hydrochloric acid; the *iodide*,  $\text{SbPhI}_2$ , forms golden-yellow needles, m. p.  $69^{\circ}$ , whilst the *chloride*, colourless needles or plates, has m. p.  $62^{\circ}$  (Hasenbäumer gives m. p.  $58^{\circ}$ , whilst Grüttner and Wiernick describe the substance as an oil). Addition of water to the alcoholic solution of the haloids causes the formation of oxyhaloids. Energetic reduction of phenylstibinic acid or phenylstibine oxide leads to the formation of *stibio-benzene*,  $\text{PhSb} \cdot \text{SbPh}$ , brown, amorphous powder, which gradually darkens above  $160^{\circ}$ , and finally softens to a black mass, and is extraordinarily susceptible to atmospheric oxidation; the properties of the product depend considerably on the mode of reduction.

which is preferably effected with sodium hypophosphite in acetone-glacial acetic acid solution.

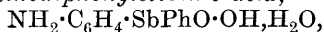
*m*-Nitrophenylstibinic acid is reduced by stannous chloride and saturated alcoholic hydrogen chloride to *m*-aminophenyldichlorostibine hydrochloride,  $\text{SbCl}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \text{HCl}$ , colourless needles, m. p.  $218^\circ$  (decomp.), which is converted by sodium iodide into *m*-aminophenyldi-iodostibine hydriodide, golden-yellow precipitate, m. p.  $160^\circ$  (decomp.). Cautious treatment with water and ammonia transforms the chloride into *m*-aminophenylstibine oxide, colourless, amorphous powder, which shrinks at about  $170^\circ$  and readily undergoes decomposition; it is oxidised by hydrogen peroxide to *m*-aminophenylstibinic acid,



(the sodium salt and the sulphate are described), which is transformed by hydrochloric acid into *m*-aminophenylstibine tetrachloride hydrochloride, colourless crystals ( $+1.5\text{H}_2\text{O}$ ), which blacken above  $190^\circ$ . (Some of these substances have been described previously by May, and the discrepancies between his data and those of the present author are due to the contamination of May's products with di- and tri-antimony derivatives.) Energetic reduction with sodium hypophosphite converts *m*-aminophenyldichlorostibine hydrochloride into *mm'*-diaminostibiobenzene, dark brown powder, which shrinks to a black mass above  $120^\circ$ , and is very readily oxidised. *p*-Chloro-*m*-aminophenyldichlorostibine hydrochloride forms colourless needles, m. p. about  $153^\circ$  (decomp.), and is converted by cold dilute ammonia into *p*-chloro-*m*-aminostibine oxide.

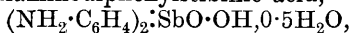
A considerable number of diarylantimony-compounds are described (compare Michaelis and Reese, A., 1886, 885; Michaelis and Günther, *loc. cit.*); the diarylstibinic acids are prepared by the oxidation of the diarylstibine oxides or by the action of antimonylaryls on diazo-compounds,  $\text{Ar}^1\text{N}_2\text{Cl} + \text{Ar}^{11}\text{SbO} + 2\text{KOH} = \text{Ar}^1\text{Ar}^{11}\text{SbO} \cdot \text{OK} + \text{N}_2 + \text{KCl}$ , the latter procedure permitting the introduction of dissimilar radicles into the acid molecule. They differ considerably from the monoarylstibinic acids in their tendency towards polymerisation, and their behaviour towards alkali does not enable such definite conclusions to be drawn as in the case of the simpler compounds.

Diphenylstibine oxide,  $\text{O}(\text{SbPh}_2)_2$ , m. p.  $78-80^\circ$ , is prepared by heating phenylstibine oxide in a current of dry carbon dioxide at  $100^\circ$ , or by the action of tartaric acid on a solution of the substance in glacial acetic acid at the ordinary temperature; it is reduced by hypophosphorous acid to a yellow compound, presumably tetraphenyldistibine,  $\text{Ph}_2\text{Sb} \cdot \text{SbPh}_2$ , converted by hydrochloric acid into chlorodiphenylstibine, m. p.  $68^\circ$ , and oxidised by hydrogen peroxide in alcoholic alkaline solution to diphenylstibinic acid, m. p. about  $285^\circ$ . *m*-Aminodiphenylstibinic acid,



from diazotised aniline and dichloro-*m*-aminophenylstibine hydrochloride in the presence of excess of alkali, is a colourless powder

which softens at about  $200^{\circ}$ , and is readily converted into the *chloride*, which gradually darkens when heated above  $200^{\circ}$ . Chloro-*mm'*-diaminodiphenylstibine hydrochloride, colourless needles, m. p.  $215^{\circ}$  (decomp.) (compare Morgan and Micklethwait, *loc. cit.*), yields hydroxy-*mm'*-diaminodiphenylstibine, which softens indefinitely above  $70^{\circ}$ , and is oxidised by hydrogen peroxide to *mm'*-diaminodiphenylstibinic acid,



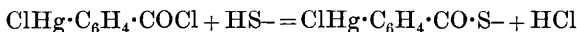
decomp. about  $230^{\circ}$  (*mm'*-diaminodiphenylstibine chloride hydrochloride remains unchanged below  $250^{\circ}$ ).

Triphenylstibine, m. p.  $53^{\circ}$ , results when phenylstibine oxide is heated in a stream of dry carbon dioxide at  $180$ — $200^{\circ}$ . Tri-*m*-aminotriphenylstibine exists in an amorphous, hydrated form ( $+0.5\text{H}_2\text{O}$ ), which softens above  $80^{\circ}$ , and a crystalline variety, m. p.  $124^{\circ}$ . The former can be converted into the latter by crystallisation from alcohol, the reverse change being effected by solution in hydrochloric acid and precipitation with ammonia.

The estimation of antimony is effected by one of the following methods. Arylstibine oxides and triarylstibines, which contain an amino-group attached to the benzene nucleus, can frequently be directly titrated with iodine in very dilute faintly acid solution. If the stibine oxide is devoid of a group conferring the property of solubility in water, a suitable bicarbonate-alkaline solution can generally be obtained with the aid of tartaric acid and organic solvents. Alternatively, about 1/1000 molecule of the substance is mixed in a Kjeldahl flask with sodium chloride (0.2 gram) and sodium hydrogen sulphate (3 grams), and boiled during an hour with a mixture of nitric acid (D 1.49; 1.5 c.c.) and concentrated sulphuric acid (10 c.c.). After cooling, ammonium sulphate (1 gram) is added, and the mixture is boiled for thirty minutes to remove nitric acid; it is subsequently diluted to about 300 c.c., and, after addition of 5*N*-hydrochloric acid (20 c.c.), is reduced with sulphur dioxide and potassium bromide. The antimony is finally estimated by titration with *N*/10-iodine in bicarbonate-alkaline solution.

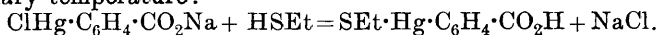
H. W.

**Action of Mercaptans and Hydrogen Sulphide on *o*-Chloromercuribenzoyl Chloride.** GEORG SACHS (*Ber.*, 1920, 53, [B], 1737—1745).—*o*-Chloromercuribenzoyl chloride can possibly react with the sulph-hydryl group in accordance with either of the schemes:

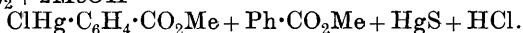
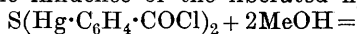


and  $\text{ClHg} \cdot \text{C}_6\text{H}_4 \cdot \text{COCl} + \text{HS}^- = \text{S}^- \cdot \text{Hg} \cdot \text{C}_6\text{H}_4 \cdot \text{COCl} + \text{HCl}$ . With mercaptans, the reaction follows the first course, with hydrogen sulphide the second. An explanation of the failure of the  $-\text{HgCl}$  group to react with mercaptans is found in the observation that whilst chloromercuribenzoic acid and phenylmercurichloride do not react with mercaptans in acetone solution, even when heated on the water-bath, sodium chloromercuribenzoate and ethyl-

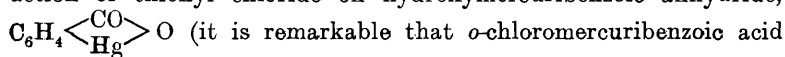
mercaptan readily yield ethylthiomercuribenzoic acid at the ordinary temperature:



Reaction therefore appears to take place only when the liberated hydrochloric acid is immediately neutralised. This circumstance, taken in conjunction with signs of ready hydrolysis of the mercapto-acids, indicates that this new class of substances is to be regarded as salts of a very weak acid, in which the specific relationship of mercury to sulphur does not play an important part. Reaction between mercaptans and phenylmercurichloride or chloromercuribenzoic acid takes place at  $150^\circ$ , and leads to rupture of the mercury-carbon bond:  $\text{ClHg}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H} + \text{HSEt} = \text{Ph}\cdot\text{CO}_2\text{H} + \text{ClHg}\cdot\text{S}\cdot\text{Et}$ . Similar fission occurs when sulphidomercuribenzoyl chloride is treated with boiling methyl alcohol; mercuric sulphide is precipitated, as is usual with this type of sulphide, and, in addition, the remainder of the molecule decomposes smoothly under the influence of the liberated hydrogen chloride.



The following substances are described: *o*-chloromercuribenzoyl chloride, needles, which melt incompletely at  $173\cdot5^\circ$ , is prepared, together with small amounts of an amorphous substance, by the action of thionyl chloride on hydroxymercuribenzoic anhydride,



does not react with thionyl chloride, whilst *o*-ethylthiomercuribenzoic acid gives chloromercuribenzoic acid and smaller amounts of highly decomposed substances); *sulphidomercuribenzoyl chloride*,  $\text{S}(\text{Hg}\cdot\text{C}_6\text{H}_4\cdot\text{COCl})_2$ , pale yellow precipitate, which does not melt below  $230^\circ$ , obtained by the interaction of chloromercuribenzoyl chloride and hydrogen sulphide in dry ethereal solution; methyl *o*-chloromercuribenzoate, m. p.  $181\cdot5\text{--}182^\circ$  (Schrauth, Schoeller, and Hueter, this vol., i, 455, give m. p.  $142\text{--}162^\circ$ ), which after some months had fallen to  $149\text{--}149\cdot5^\circ$ , and could not then be restored to its original value; *ethyl o*-chloromercurithiobenzoate,  $\text{ClHg}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{SEt}$ , yellow, microscopic, rhombic leaflets, m. p.  $142\cdot5\text{--}144\cdot5^\circ$ ; ethylthiomercurichloride; *ethylthiomercuribenzoic acid*, m. p.  $138\cdot5\text{--}140^\circ$  to a turbid liquid, which immediately blackens, owing to separation of mercuric sulphide.

H. W.

### Mercury Derivatives of Substances with Multiple Bonds.

IV. W. MANCHOT, F. BÖSSENECKER, and F. MÄHRLEIN (*Annalen*, 1920, 421, 316—330).—The mercuration of benzene derivatives which contain a double bond in the side-chain has been investigated; the results obtained are similar to those recorded with ethylene (this vol., i, 720), and thus further confirm the authors' conclusion that these substances are to be regarded as additive compounds.

Safrole is readily dissolved by aqueous mercuric acetate solution at  $50^\circ$ , and the product is converted by aqueous sodium chloride into the substance,  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{HgCl}\cdot\text{OH}$ , colourless,

well-defined, stable, monoclinic prisms, m. p.  $136-137^{\circ}$ , which is immediately decomposed by dilute hydrochloric acid, with regeneration of safrole; the corresponding *bromide*, colourless, silky needles, m. p.  $144-145^{\circ}$ , and the *iodide*, slender needles, m. p.  $152.5^{\circ}$ , are similarly prepared. The mercury atom is comparatively firmly retained in all these compounds. The free *base* is readily obtained in aqueous solution by the action of silver oxide on the bromide; it is faintly alkaline to litmus, but does not give a coloration with phenolphthalein. In a similar manner, eugenol methyl ether yields the *compound*,  $C_{11}H_{15}O_3 \cdot HgCl$ , colourless needles, m. p.  $112.5^{\circ}$ , but the preparation is rendered unusually difficult by the formation of smeary masses. Eugenol itself, on the other hand, does not yield a well-defined product when molar proportions of the components are taken; when, however, three molecules of mercuric acetate react with one molecule of eugenol, a very sparingly soluble *product* is obtained, which contains two atoms of mercury (a similar *substance* can also be prepared from safrole). Mercuration of phenylethylene gives more complex products, investigation of which is not quite completed; it is, however, established that addition of basic mercury salts occurs, and that the products, in part at any rate, do not retain the mercury firmly. Styrenes, which contain a terminal methyl group in the side-chain (*isosafrole*, *isoeugenol*), behave differently, causing reduction of the mercury salt, as does  $\beta$ -methylbutylene.

Estimation of mercury is conveniently effected as follows. The substance is gently boiled under a reflux condenser with hydrochloric acid (20%; 20 c.c.) and concentrated hydrogen peroxide (3 c.c.) during three to four hours. Organic matter is removed by filtration, and the residue is thoroughly washed. The mercury is precipitated in the filtrate by hydrogen sulphide. The precipitated mercuric sulphide is collected in a Gooch crucible, and freed from organic matter and uncombined sulphur by being washed successively with hot water, alcohol, pyridine, alcohol, warm carbon disulphide, alcohol, and ether; it is dried at  $110^{\circ}$  until constant in weight. The process gives very accurate results, and shows that the high values obtained previously are mainly due to contamination of the mercuric sulphide by organic matter.

H. W.

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### Physiological Chemistry.

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**A Method for the Graphic Representation of Chemical Compounds and Reactions.** OTTO LIESCHE (*Biochem. Zeitsch.*, 1920, **105**, 282—304).—A theoretical paper dealing with the application of the graphic representation of chemical compounds and reactions to biochemistry. S. S. Z.

**Catalysis. VII. Temperature-coefficient of Physiological Processes.** NIL RATAN DHAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 44—49).—Physiological processes take place mostly in heterogeneous media. The Brownian movement of the colloid particles present in the reacting substances does away with the diffusion layer characteristic of heterogeneous reactions, and makes the physiological reactions similar to positively catalysed reactions taking place in homogeneous media. Consequently, the temperature-coefficients of physiological processes, instead of being small (about 1.2), are usually greater than 2 for a rise of 10°. The spontaneous destruction of certain toxins is greatly influenced by temperature, a factor of importance in fever, when the poison is destroyed very rapidly. Before the destructive effect of temperature sets in, the Arrhenius formula connecting temperature and reaction velocity is generally applicable to physiological processes (compare A., 1919, ii, 404). J. R. P.

**The Presence of Glycuronic Acids in Human Blood. Preliminary Note.** WILHELM STEPP (*Zeitsch. physiol. Chem.*, 1919, **107**, 264—268).—Several samples of blood from normal, diabetic, and nephritic patients were examined for glycuronic acid by the naphtharesorcinol reaction. All the samples examined gave a positive reaction, the blood of the nephritic patients in the azotæmia stage giving the most intense coloration. The reaction in the case of the diabetics showed varying intensity. The orcinol and phloroglucinol reactions were also employed in the latter case. S. S. Z.

**The Reducing Substances of Blood. Comparative Estimations of "Blood Sugar" by means of Reduction, Polarisation, and Fermentation in Several Cases of Diabetes and Nephritis.** WILHELM STEPP (*Zeitsch. physiol. Chem.*, 1919, **107**, 29—44).—Estimations of blood sugar in the blood of diabetic and nephritic patients with Lohnstein's "precision fermentation saccharimeter" give figures similar to those obtained by polarimetric estimations. As the reducing power shown by blood is always in excess of that theoretically required by the amount of blood sugar estimated polarimetrically, it is to be deduced that reducing substances other than dextrose are responsible for this. Certain samples of blood of diabetic patients, when concentrated, give a lower reducing value than the equivalent quantity of original blood, which suggests that some of the reducing substances are volatile. In one instance, the reduction of Fehling's solution by the distillate has actually been established. As the concentrated blood samples still show a higher reducing power than that expected from the polarisation and fermentation figures, it may be assumed that, besides volatile, there are non-volatile reducing substances in blood which cannot be identified with dextrose. S. S. Z.

**The Physiological Distribution of Sugar in Plasma and Corpuscles.** R. BRINKMAN and (FRL.) E. VAN DAM (*Biochem. Zeitsch.*, 1920, **105**, 93—95).—The erythrocytes of human and frog's blood do not contain sugar; they only become permeable to it after the blood has clotted. Corpuscles, however, in blood which is prevented from clotting by sodium fluoride, oxalate, or hirudin become permeable to sugar. This is explained by the fact that the early phases of clotting are not hindered by these reagents.  
S. S. Z.

**The Nomenclature of the so-called Accessory Food Factors (Vitamins).** JACK CECIL DRUMMOND (*Biochem. J.*, 1920, **14**, 660).—It is suggested that the name vitamin be employed for these unidentified substances, and that they be individually referred to as vitamin-A, -B, -C, etc. Dropping the final "e" in the original word vitamine, introduced by Funk, removes the objections to that word.  
J. C. D.

**Researches on the Fat-soluble Accessory Substance. III. Technique for carrying out Feeding Tests for Vitamin-A (Fat-soluble-A).** JACK CECIL DRUMMOND and KATHARINE HOPE COWARD (*Biochem. J.*, 1920, **14**, 661—664).—Great care should be employed to ensure that the basal diet is free from this vitamin.  
J. C. D.

**Researches on the Fat-soluble Accessory Substance. V. The Nutritive Value of Animal and Vegetable Oils and Fats Considered in Relation to their Colour.** JACK CECIL DRUMMOND and KATHARINE HOPE COWARD (*Biochem. J.*, 1920, **14**, 668—677).—No hard-and-fast line can be drawn between the animal and vegetable oils and fats when their value as a source of vitamin-A is considered. As a class, the animal fats are superior in this respect to the vegetable oils, but some members of the latter class, for example, palm oil, may be valuable sources of the vitamin. The presence of lipochrome pigments cannot be regarded as a certain indication of the presence of the vitamin-A. The nutritive value of an animal oil is largely dependent on the diet which the animal has received. Both animal and vegetable oils and fats probably lose vitamin during purification and refining.  
J. C. D.

**Cuorin.** HUGH MACLEAN and WILLIAM JAMES GRIFFITHS (*Biochem. J.*, 1920, **14**, 615—617).—Cuorin, described by Erlandsen (A., 1907, i, 371), is not a chemical unit, but results from decomposition taking place in the tissues during the processes utilised for the extraction of the lipins.

The only phosphatides present in animal tissues are lecithin, kephalin, and sphingomyelin.  
J. C. D.

**Primary and Secondary Phenol Reaction. Mutual Antagonism of  $\alpha$ -Naphthol and  $p$ -Phenylenedimethyldiamine in Daphnideæ.** W. LOELE (*Zentr. allg. Pathol. pathol. Anat.*, **30**, 614—617; from *Chem. Zentr.*, 1920, iii, 493).—Accord-



ing to Gierke and Graeff, naphthol dissolves the labile oxydases (protective colloids of the muscles against foreign substances). These oxydases, which are probably cyclic amines with aldehydic character, are termed aldamines by the author. They are particularly noticeable where the cells have a markedly protective character. They may be classified as: (1) primary aldamines (*a*) yielding the naphthol reaction without treatment with formaldehyde, and (*b*) giving a positive naphthol reaction only after addition of formaldehyde, and (2) secondary aldamines showing (*a*) granular reaction, and (*b*) nucleus reaction. Substances belonging to the first group are found in the granula of  $\alpha$ - and  $\delta$ -leucocytes and in the cell of the snail, and do not appear to be associated with any particular form of cell. Members of the sub-group, *b*, are present in the mucus cells of the black snail. The secondary aldamines, which are formed by the action of primary aldamines, have the greater importance.

H. W.

**The Distribution of Inorganic Iron in Plant and Animal Tissues.** HENRY WALLACE JONES (*Biochem. J.*, 1920, **14**, 654—659).—By microchemical methods, the author has traced the occurrence of inorganic iron in a large number of organisms. Inorganic iron is more widely distributed throughout animal and plant tissues than is generally realised, and the lower organisms in both cases give the reaction more markedly than the higher ones. Aquatic animals contain more than land animals, and foetal tissues are richer than adult tissues.

J. C. D.

**Biochemical Studies on Marine Organisms. I. The Occurrence of Copper.** WILLIAM C. ROSE and MEYER BODANSKY (*J. Biol. Chem.*, 1920, **44**, 99—112).—Numerous analyses are recorded, and it is believed that copper is a normal, and possibly an essential, constituent of marine animals.

J. C. D.

**The Distribution of Zinc in the Organism of the Horse.** GABRIEL BERTRAND and R. VLADESCO (*Compt. rend.*, 1920, **171**, 744—746).—All the organs and tissues of the horse contain notable proportions of zinc, the amounts found varying from 3—36 mg. per 100 grams of fresh material. Not only does the amount of zinc vary considerably from one organ or tissue to another, but also from one animal to another.

W. G.

**Excretion of Formic Acid from the Human Organism after the Administration of Methyl Alcohol, Hexamethylenetetramine, Sodium Formate, Sodium Lactate, and Dextrose.** W. AUTENRIETH (*Arch. Pharm.*, 1920, **258**, 15—33).—Formic acid is a normal and fairly constantly occurring constituent of human urine, varying in quantity within somewhat wide limits with different individuals and with varying diet, but from 0.5—0.65 gram per forty-eight hours, or an average of about 0.28 gram per day, may be regarded as a normal amount. Adminis-

tration of methyl alcohol causes a notable increase in the formic acid excreted, particularly on the third and fourth day following, the total excess over the normal representing about 5% of the methyl alcohol taken. The mere presence of formic acid in the urine is accordingly insufficient to establish methyl alcohol poisoning. In such a case, a quantitative examination indicating something of the order of 1 gram of formic acid per day is essential. In no case was formaldehyde found in the urine after the administration of methyl alcohol, although possibly traces of the latter might be found unchanged. This, together with the fact that, after the administration of hexamethylenetetramine (urotropine), large quantities of formaldehyde, but no increase in the amount of formic acid, were found in the urine, shows that formaldehyde is not, as has been supposed, an intermediate product of oxidation in the animal organism. Formic acid, administered as its sodium salt, underwent partial combustion, 18% only being found unchanged in the urine. Neither sodium lactate nor dextrose caused any abnormal increase in the excretion of formic acid, even when administered in large quantities. G. F. M.

#### **The Physical Theory of Pharmacological Actions.**

I. TRAUBE (*Biochem. Zeitsch.*, 1920, **105**, 115—116).—A reply to Heubner (this vol., i, 791). S. S. Z.

**The Narcosis Theory.** ERICH KNAFFL-LENZ (*Biochem. Zeitsch.*, 1920, **105**, 88—92).—A reply to Winterstein (A., 1917, i, 68) and Traube (*Pflüger's Archiv*, 1919, **176**, 72). S. S. Z.

**Fate of  $\beta$ -Naphthylamine in the Organism of the Dog.** ENGEL (*Zentr. Gewerbehyg. Unfallverhüt.*, **8**, 816; from *Chem. Zentr.*, 1920, iii, 495).— $\beta$ -Naphthylamine hydrochloride (1.0 and 0.5 gram) was administered to two dogs which were in a condition of nitrogen equilibrium and had a constant nitrogen and sulphur elimination. Signs of illness were not observed. After the injection, the amounts of ethylsulphuric acid and glycuronic acid in the urine were increased, and this lasted for five to six days. The ratio of the two acids indicated that much the greater part of the amine is eliminated in conjunction with the ethylsulphuric acid, at any rate in the case of carnivorous animals. In one experiment with a carbohydrate diet, only one-fourth of the amine was associated with ethylsulphuric acid, the remainder with glycuronic acid. The increment in the amounts of the two acids eliminated, amounted in one experiment to 0.725 and 0.486 gram respectively. Assuming that only aminonaphthols are formed, this would correspond with 1.444 grams of  $\beta$ -naphthylamine, which is more than was actually administered; it appears, therefore, that dihydroxynaphthylamines are also formed. Unchanged  $\beta$ -naphthylamine could not be detected in the urine. H. W.

**A Toxicological Study of some Alcohols, with especial reference to Isomerides.** DAVID I. MACHT (*J. Pharm. expt. Ther.*, 1920, **16**, 1—10).—The toxicity of the normal aliphatic

alcohols, methyl, ethyl, butyl, and amyl, increases with their place in the homologous series.

Secondary propyl, butyl, and amyl alcohols were found to be less toxic than the corresponding primary alcohols.

In discussing the toxicity of alcohols, a distinction should be drawn between the acute or immediate, and the secondary or remoter, effects of the drugs.

J. C. D.

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## Chemistry of Vegetable Physiology and Agriculture.

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**The Production of Acetaldehyde by certain Pentose Fermenting Bacteria.** W. H. PETERSON and E. B. FRED (*J. Biol. Chem.*, 1920, **44**, 29—46).—In the fermentation of carbohydrates by three types of pentose-fermenting organisms (an organism related to the colon-aerogenes group, *Bacillus acetoethylicum*, and *Lactobacillus pentoaceticus*), acetaldehyde is produced when a fixative, such as sodium or calcium bisulphite, is added. The maximum yield is from xylose, but the amount found is proportional to the amount of fixative added. The production of acetaldehyde is correlated with the production of alcohol. An increase in the former results in a decrease in the latter. The production of acetaldehyde is associated with a high production of volatile acid. These results illustrate the intimate relations which exist between the balanced processes of oxidation and reduction in the fermenting solution.

The production of acetaldehyde by the acetone-forming organism, *B. acetoethylicum*, is of particular interest, since it is possible that, through condensation of the aldehyde and subsequent processes of oxidation and decarboxylation, the acetone is formed.

An attempt to correlate the production of acetaldehyde with Neuberg's theory, that pyruvic acid is an intermediate product in sugar fermentation, did not give conclusive results. Pyruvic acid and its sodium salt are fermented to a greater or less extent by all three types of bacteria. Among the products formed are carbon dioxide, hydrogen, and a volatile acid. These products were also formed when pyruvic acid was fermented in the presence of sodium sulphite, but no trace of acetaldehyde was found. J. C. D.

**New Methods of Analysis of Hydrocarbons with the Aid of Bacteria.** JENÖ TAUSZ and MARTA PETER (*Centr. Bakt. Par.*, 1919, II, **49**, 497—554).—The authors have isolated from garden soil three new bacteria, namely, *Bacterium aliphaticum*, *B. aliphaticum liquefaciens*, and *Paraffin bacterium*. The actions of these bacteria on pure synthetic hydrocarbons and on mixtures

of paraffins and naphthenes have been investigated, the hydrocarbons tested comprising *n*-hexane, *n*-octane,  $\beta\eta$ -dimethyloctane, hexadecane, triacontane, and tetratriacontane; *n*-hexylene, *n*-octylene, and hexadecylene; *cyclohexane*, *methylcyclohexane*, 1:3-dimethyl*cyclohexane*, 1:3:4-trimethyl*cyclohexane*, and *tricyclodecane*; benzene, toluene, *m*- and *p*-xylenes. The hydrocarbons were used as the sole source of carbon in solutions of inorganic nutrient materials.

*B. aliphaticum* attacks all the paraffins mentioned, and also *n*-octylene and hexadecylene, but not *n*-hexylene, naphthenes, or aromatic hydrocarbons. *B. aliphaticum liquefaciens* behaves exactly similarly. The *Paraffin bacterium* attacks hexadecane, triacontane, tetratriacontane, and hexadecylene, but not *n*-hexane, *n*-octane, hexylene, octylene, naphthenes, or benzene derivatives. The hydrocarbons attacked are destroyed completely by the bacteria, even when unattacked naphthenes are present. The organisms were employed in the analyses of various mixtures of hydrocarbons.

T. H. P.

**Inhibitory Action of Paratyphoid Bacilli on the Fermentation of Lactose by *Bacillus coli*. I.** THEOBALD SMITH and DOROTHEA E. SMITH (*J. Gen. Physiol.*, 1920, **3**, 21—33).—Bacteria of the paratyphoid group can be divided into two classes, according to whether they inhibit the formation of gas from lactose by *Bacillus coli* or not. The production of acid is not interfered with. The experiments support current theories, which hold that the acid-producing and gas-producing entities in cultures are distinct.

J. C. D.

**Production of Indole by the Pfeiffer Bacillus.** MARCEL RHEIN (*Compt. rend. soc. biol.*, 1919, **82**, 138—139).—The production of indole (mauve colour with dimethylaminobenzaldehyde and hydrochloric acid, violet tint with formaldehyde and sulphuric acid, blue colour with sodium nitroprusside, potassium hydroxide, and acetic acid), with accompanying characteristic odour, was noted in the case of abundant cultures of the Pfeiffer bacillus, but not detected in all cases.

CHEMICAL ABSTRACTS.

**Synthesis of Tryptophan by certain Bacteria and the Nature of Indole Formation.** WILLIAM JAMIESON LOGIE (*J. Path. Bact.*, 1920, **23**, 224—229).—Certain gram-negative bacilli have the power to synthesise tryptophan when growing in protein-free media. This is in support of the view of the vegetable nature of bacteria. The addition of dextrose to a living culture of *Bacillus coli* causes the rapid disappearance of the indole already formed. This seems to indicate that the effect of the dextrose is to cause increased demand for indole on the part of the organism, and not merely, by the development of acidity, to prevent the splitting off of indole from the peptone. On this hypothesis, indole "formation" is a consequence rather of diminished use of indole

as tryptophan than of special formation by the organism. The splitting off of indole appears to be a reversible chemical change.

The difference between *B. coli* and *B. typhosus* with respect to indole formation on re-absorption is most probably due to the fact that *B. coli* possesses an enzyme which enables it to split off and utilise the open-chain (alanine) portion of the tryptophan molecule.

J. C. D.

### **The Effect of Certain Environmental Conditions on the Rate of Destruction of Vanillin by a Soil Bacterium.**

WILLIAM J. ROBBINS and A. B. MASSEY (*Soil Sci.*, 1920, 10, 237—246).—The particular bacterium used was one from an Alabama soil. In culture solutions, very slight concentrations of hydrochloric acid inhibited its action on vanillin, but the bacterium was not so sensitive to alkali. Aeration favoured the destruction of vanillin by the organism. In culture solutions containing calcium superphosphate, sodium nitrate, and potassium sulphate, either singly or in combination, the organism was most active in those solutions rich in calcium superphosphate and least active in the solutions rich in potassium sulphate. The presence of dextrose had no marked effect on the rate of destruction of vanillin by the organism.

W. G.

### **Yeast Nutrition and Fermentation. Does Development of Yeast Occur without Fermentation of Sugar?**

TH. BOKORNY (*Centr. Bakt. Par.*, 1920, ii, 50, 23—33).—The author finds that it is possible for considerable increase of yeast to occur in solutions containing no trace of sugar. Besides the ordinary fermentable sugars, rhamnose, arabinose, lactose, peptone, asparagine, and other amides, tartaric, acetic, and citric acids, and, under certain conditions, glycerol, all serve to supply yeast with the carbon necessary for its growth. Between the nitrogenous constituents of the nutrient solution and the fermentation of the sugar present, the sole connexion existing is that plentiful and suitable nitrogenous nutrition gives rise to much yeast, and thus to much zymase. Fermentation is not, at any rate when access of air is permitted, a vital necessity for yeast, but it is of advantage in that it retards the development of bacteria, and, further, brings the yeast into increased contact with the nutrient materials of the liquid.

T. H. P.

### **Is Fermentation of Sugar by Yeast due Solely to Zymase?**

J. GIAJA (*Compt. rend. soc. biol.*, 1919, 82, 804—806).—Yeast lost 86% and 94% of its fermentative power when treated with toluene for thirty and sixty minutes, respectively, after attaining its maximal fermentative activity in the presence of sugar. The residual 6% of "zymase" (which remained practically intact for a long time) is practically identical in amount with that possessed by yeast treated as above during rest. Yeast from which the enveloping membrane had been dissolved by the action of the

digestive fluid of *Helix pomatia* likewise lost most of its fermentative power when treated with toluene. The above loss of fermentative power cannot plausibly be attributed to destruction of zymase by the action of endotrypsin as suggested by Buchner. The author concludes that only approximately 5% of the fermentative activity of yeast can be attributed to zymase. CHEMICAL ABSTRACTS.

**The Effect of Pyruvates, Aldehydes, and Methylene-blue on the Fermentation of Dextrose by Yeast Juice and Zymin in the Presence of Phosphate.** ARTHUR HARDEN and FRANCIS ROBERT HENLEY (*Biochem. J.*, 1920, **14**, 642—653).—The facts that the activating effect both of  $\alpha$ -keto-acids and of aldehydes is chiefly manifested at the commencement of the reaction, and that the experiments both of Oppenheimer (A., 1915, i, 358) and Neuberg (A., 1915, i, 1043; 1918, i, 469) were made with maceration extracts which contain a large amount of mineral phosphate, and that the effect was less marked with lævulose than with dextrose, led the authors to inquire whether the action was a general stimulation of the fermentation process or a more specific acceleration of the reaction in presence of free mineral phosphate.

It has been found that an aldehyde when added to fermenting mixtures of yeast juice or zymin (acetone yeast) with dextrose induces no acceleration in the normal rate of fermentation. In the presence of a suitable amount of phosphate, the effect of the aldehyde is greatly to diminish the time required for the attainment of the maximum, so that the volume of gas evolved in the period immediately following the addition of phosphate is greatly increased. At the same time, a considerably higher maximum is attained. On completion of the esterification of the phosphate, the rate again diminishes, both in the presence and absence of an aldehyde, and the total evolution is not greatly different in the two cases. Similar phenomena are produced by pyruvates.

The striking action of the aldehydes suggests that the cause of the delay in attainment of the maximum after the addition of the phosphate was lack of an acceptor for hydrogen. In order to test this idea, methylene-blue was substituted for aldehyde, with the result that it was found to produce a very similar effect.

The rôle of the hydrogen acceptors in the fermentation is discussed. It is probable that the hydrolysis of the hexosephosphate, both that originally present and that slowly formed in the fermenting mixture, results in the formation of lævulose, which in its turn yields a hydrogen acceptor, and thus assists the increase in the rate of fermentation.

J. C. D.

**A New Fixation Method and its Application in Alcoholic Fermentation.** CARL NEUBERG and ELSA REINFURTH (*Biochem. Zeitsch.*, 1920, **106**, 281—291).—The authors have utilised Vorländer's observation that dimethylcyclohexanedione reacts with acetaldehyde, yielding ethylidenebisdimethylcyclohexanedione, for the fixation of acetaldehyde in the fermentation of sugar. In order to isolate the product, the yeast was centri-

fused and extracted with hot alcohol. The alcoholic extract was concentrated and added to much water, when ethylidenedisdimethylcyclohexanedione was precipitated (m. p. 139—140°), and its nature confirmed by conversion into its anhydride,  $C_{18}H_{24}O_3$ , m. p. 173—175°, by heating with glacial acetic acid under reflux. Acetaldehyde can also be fixed in the above way when the sugar is fermented with maceration juice. Pyruvic acid is not fixed by dimethylcyclohexanedione. S. S. Z.

**The Three Forms of the Fermentation of Sugar. Their Connexion and their Balance Sheet.** CARL NEUBERG, JULIUS HIRSCH, and ELSA REINFURTH (*Biochem. Zeitsch.*, 1920, 105, 307—336).—The relation of the three forms of fermentation (this vol., i, 798) was studied by estimating the quantity of fermented sugar and the products of fermentation at various periods of the processes. In all the three forms, the common product, acetaldehyde, is produced, which is reduced to alcohol in the first form of fermentation, is fixed by the sulphite in the second form of fermentation, and is converted into acetic acid and alcohol in the third "dismutation" form of fermentation. In all the three forms of fermentation, the fermented sugar was accounted for in the products of fermentation, which were produced in definite proportions. S. S. Z.

**The Physical-chemical Conception of the Processes of Fermentation.** WOLFGANG OSTWALD (*Biochem. Zeitsch.*, 1920, 105, 305); C. NEUBERG (*ibid.*, 306).—Polemical. S. S. Z.

**Influence of Fluctuating Barometric Pressure on the Course of Alcoholic Fermentation and of Biological Processes in General.** AUGUST RIPPEL (*Centr. Bakt. Par.*, 1917, ii, 47, 225—229).—In certain cases, it is found that the curve showing the periodic evolution of carbon dioxide from a fermenting solution exhibits a zig-zag course, high barometric pressure corresponding with low rate of fermentation, and vice versa. When the nutrient solution employed is such that a vigorous fermentation is rapidly established, the effect of the barometric pressure may not be evident in the early stages, but it becomes apparent when the action slackens. Such increased liberation or retention of gases, which are either merely present as such or represent the final products of a biological or chemical process, may have important effects on biological processes. T. H. P.

**Comparative Studies on Respiration. XII. A Comparison of the Production of Carbon Dioxide by *Penicillium* and by a Solution of Dextrose and Hydrogen Peroxide.** F. G. GUSTAFSON (*J. Gen. Physiol.*, 1920, 3, 35—39).—A neutral solution of dextrose and hydrogen peroxide acts like *Penicillium chrysogenum* in producing an increased amount of carbon dioxide on the addition of acid, but not on the addition of alkali.

J. C. D.



**Attackability of *cis*- and *trans*-Isomeric Unsaturated Acids by Moulds.** P. E. VERKADE and N. L. SÖHNGEN (*Centr. Bakt. Par.*, 1920, ii, **50**, 81—87).—In solution containing excess of undissolved calcium carbonate, these acids exhibit the same behaviour towards *Aspergillus niger* as towards *Penicillium glaucum*; fumaric, cinnamic, *allocinnamic*, aconitic, oleic, and erucic acids are assimilated readily, and glutaconic acid slightly, whereas maleic, citraconic, mesaconic, itaconic, phenylitaconic, *isocrotonic*, crotonic,  $\beta\beta$ -dimethylacrylic, angelic, tiglic, undecenoic, elaidic, and brassidic acids are not attacked. Similar results are obtained when the free acids instead of their calcium salts are employed, excepting that with cinnamic acid no development of the two organisms takes place. It is evident that the attackability or non-attackability by mould fungi is inadmissible as a means of distinguishing between *cis-trans*-isomerides.

The behaviour of certain of these acids towards the moulds is explainable by their solubilities in water and in olive oil (compare Waterman, *ibid.*, 1915, II, **42**, 639), but that of other acids cannot be explained in this way. Assimilability or non-assimilability appears, indeed, to be dependent principally on the molecular configuration of the compound. T. H. P.

**Favourable Influence of Selenium on some Moulds coming from the Cheese Industry.** ANTONIN NĚMEC and VÁCLAV KÁŠ (*Compt. rend.*, 1920, **171**, 746—748).—With selenium in the form of sodium selenate, there is an increase in the weight of dry mycelium in the case of *Penicillium Roqueforti*, with increasing amounts of sodium selenate in the culture solution. With *P. candidum*, a toxic effect was noticed when the amount of sodium selenate increased beyond a certain limit. The ash content of the mycelium increased at first with the amount of selenium present, but reached a maximum and then diminished. W. G.

**Specific Disinfection Processes. II. Action of Salts and Ions on Bacteria.** PHILIPP EISENBERG (*Centr. Bakt. Par.*, 1918, i, **82**, 69—208).—The author has carried out extensive series of experiments on the effects of inorganic salts in different concentrations on the development in peptone-meat extract-agar or bouillon of six gram-positive and six gram-negative bacterial species. The results are given in detail, and lead to the following, among other, conclusions. The toxicity of salts may be regarded as an additive function of their component ions, although purely molecular actions are not to be excluded. The commoner anions (cations) may be arranged in toxicity series, which vary appreciably for different cations (anions). The normal life functions of bacteria are connected with a state of swelling of the protoplasmic colloids definite for each species, and any deviation from this state in either direction may cause disturbance of these functions, or even death, of the bacteria; hence the toxicity of salts increases with their swelling properties, and also with their precipitating action on bacteria. The effects of salts on the gram-specificity of bacteria are discussed.

Various cases of species- or group-specificity are indicated. In evaluating antiseptics, it is necessary to employ a number of representative bacterial species. T. H. P.

**Regularities in the Preservation of Wood. Poisoning Action of Inorganic Compounds (Salts) on Fungi.**

FRIEDRICH MOLL (*Centr. Bakt. Par.*, 1920, ii, 51, 257—279).—

The author has investigated a series of 130 different salts with respect to the effect they produce, in various concentrations, on a culture of *Penicillium glaucum* on a peptone-agar medium. The results obtained show that the poisonous action of salts is an additive property of the ions. In the order of diminishing activity, the poisonous ions are: mercury, silver, cadmium, cyanogen, copper, zinc, iron, cobalt, chromium, fluorine. Most acid ions and the ions of the alkali and alkaline earth metals, magnesium, and aluminium may be regarded as inactive in this respect. The poisonous action depends on the solubility in water of the salt and on its decomposition into ions in the aqueous solution. Every ion exhibits a specific poisonous action, and complex ions, such as the chromate and fluosilicic ions, must be regarded as independent individuals, their activity being equal to, or smaller, or greater than, the sum of their constituents. Addition of other salts to active substances may affect the time-course of the disinfection, but does not alter the final result. The activity of a given amount of a soluble salt or mixture of salts depends only on the quantity of active constituents present and on their specific effects. T. H. P.

**Toxicity and Chemical Potential.** W. LASH MILLER

(*J. Physical Chem.*, 1920, 24, 562—569).—The toxicity of a solution containing phenol and an indifferent salt depends primarily on the chemical potential of the phenol in the solution. Two solutions have the same toxicity when they are in equilibrium with the same solution of phenol in an immiscible solvent, such as toluene or petroleum. Complications may arise from the toxicity of the salts themselves, or in dilute solutions from the plasmolysis of the cell, independently of the toxicity of the solutions employed. One or two individual cases which do not fall under these heads are worthy of further study. The observation of Paul and Krönig that solutions of mercuric chloride in aqueous alcohol show a maximum of toxicity when the ratio of alcohol to water in the solution is 1 to 3 affords another illustration of the principle, since Laird has shown that the solubility of mercuric chloride in aqueous alcohol passes through a minimum at the same ratio. J. R. P.

**The Toxicity towards Anthrax and Staphylococcus of Solutions containing Phenol and Sodium Chloride.**

J. S. LEMON (*J. Physical Chem.*, 1920, 24, 570—584).—Experiments with anthrax spores showed that the increased toxicity of phenol observed when sodium chloride is added to its solution is in accordance with the assumption that two solutions of phenol, with

or without salt, are equally toxic if their compositions are such that both would be in equilibrium with the same solutions of phenol in toluene. Experiments with *Staphylococcus*, in which lower concentrations of phenol were used, showed that whilst the assumption is in fair accord with the behaviour of 0.80% phenol, in the case of 0.60% phenol, the chemically equivalent solution containing salts is much less toxic; 0.70% phenol occupies an intermediate position.

J. R. P.

### Disinfecting Values of the Three Isomeric Cresols.

FRITZ DITTHORN (*Centr. Bakt. Par.*, 1919, i, **82**, 483—491).—Experiments made with suspensions of *Bacillus coli*, *B. pyocyaneus*, and *Staphylococcus* in sodium chloride solution and in bouillon show that *m*-cresol outstrips its two isomerides in germicidal power, which is not very marked in the salt and bouillon suspensions, but is considerable in liquids containing proteins (ascites). Of the two other isomerides, the ortho-compound possibly has a slightly greater action than the para-compound. In practice, 2—2.5% solutions of a mixture of the isomerides are used, and the differences observed are then of little importance, the germicidal powers of 0.75—1.0% solutions of the three compounds being almost identical.

T. H. P.

### Organic Carbon Nutrition of Plants. Parallels between Fungi and Green Plants.

TH. BOKORNY (*Centr. Bakt. Par.*, 1917, II, **47**, 191—224, 301—375).—The author gives a summary of the observations made by various investigators with reference to the use by fungi and green plants of compounds of the following classes: alcohols, phenols, aldehydes, ketones, ketonic esters, organic acids, carbohydrates, amino-compounds, and cyanogen derivatives.

T. H. P.

### Reduction of Nitric Acid in Green Cells.

OTTO WARBURG (*Naturwiss.*, 1920, **8**, 594—596; from *Chem. Zentr.*, 1920, iii, 487).—Attempts to accelerate catalytically the reduction of nitric acid by *Chlorella vulgaris*, Beyerinck, by the use of concentrated nitrate solutions were unsuccessful, but signs of acceleration were noted in dilute solutions of free nitric acid. In an acidic nitrate mixture (*N*/100- $\text{HNO}_3$ , *N*/10-nitrate), the reduction of nitric acid amounts to 50% in the dark and to 150% in the presence of light of the total metabolism. In the former case, reaction occurs according to the equation  $\text{HNO}_3 + \text{H}_2\text{O} + 2\text{C} = \text{NH}_3 + 2\text{CO}_2 + 162,000 \text{ cal.}$  Under the action of light, the process is complicated by the assimilation of carbon dioxide, which, however, can be excluded by use of narcotics.

H. W.

### Possible Formation of Hexamethylenetetramine in Assimilating Plants, and a Microchemical Reaction for Ammonium Salts.

C. VAN ZILJP (*Pharm. Weekblad*, 1920, **57**, 1345—1348).—The combination of formaldehyde with ammonium salts in neutral, or even weakly acid, solution is found to give salts

of hexamethylenetetramine, in the same way as the base itself is formed by combination of the aldehyde with free ammonia; hence it is likely, since both formaldehyde and ammonium salts are present in growing plants, that salts of hexamethylenetetramine are also formed in the plant. The iodine-potassium iodide reagent employed by the author in the microchemical identification of hexamethylenetetramine is found to be suitable also for its salts. The test will detect 0.3 mg. of hexamethylenetetramine, and half this quantity of ammonium salt. It is therefore an extremely sensitive test for ammonium salts, and has the advantage that potassium salts do not interfere. The limit of sensitiveness is beyond the degree of solubility even of magnesium ammonium phosphate, since if a drop of formalin is added to a drop of water in which this substance is suspended, the residue, after drying, gives the characteristic brown crystals with the iodine-potassium iodide solution. It is suggested that the ammonia is withdrawn from the phosphate molecule by the aldehyde, leaving the phosphate,  $\text{MgHPO}_4$ . S. I. L.

**The Factors which Interfere with the Use of Yeast as a Test Organism for the Antineuritic Substance.** GERALDO DE PAULA SOUZA and E. V. MCCOLLUM (*J. Biol. Chem.*, 1920, **44**, 113—129).—The observations made by the authors lead them to conclude that the use of yeast as a test organism for determining the presence or absence of the vitamin-B is complicated by so many disturbing factors as to make it of little, if any, value.

J. C. D.

**Silver-reducing Cell-substances in the Leaves of Non-conifers.** FRIEDRICH CZAPEK (*Ber. Deut. bot. Ges.*, 1920, **38**, 246—252).—Molisch (*Sitzungsber. Akad. Wiss. Wien, Math. nat. Kl.*, 1918, I, **127**, 449) has shown that a 0.1—1% silver nitrate solution produces in the epidermis, especially of leaves of flowering plants, a deep black coloration of the chloroplasts; this reaction he ascribes to the presence of an extremely labile substance, which loses its reducing power even when the chlorophyll plasma dies. If the views expressed by Molisch were accurate, this reaction would represent a new "life reaction."

According to the author, however, it appears demonstrable that the cause of the silver reduction of the chloroplasts is to be sought in the presence of various depsides, which are probably not connected with the process of assimilation of carbon dioxide.

T. H. P.

**The Preparation of Phosphatides from Coloured Plant Organs.** R. FRITSCH (*Zeitsch. physiol. Chem.*, 1919, **107**, 165—175).—Various plants containing chlorophyll and other plant pigments have been examined for their phosphatide content. Only a small part of the total phosphorus could be traced to the phosphatides of the plants. In the leaves of the maple, the

phosphatide phosphorus amounted to 4.78%; in the leaves of the ash to 3.46% of the total phosphorus. No calcium inosinate was found in the green assimilating organs. In order to obtain phosphatides with the theoretical content of phosphorus, large quantities of tissue must be employed. In grass stored in silos, the phosphatides are almost entirely decomposed. S. S. Z.

**Oxidising Enzymes. II. The Nature of the Enzymes Associated with Certain Direct Oxidising Systems in Plants.** MURIEL WHELDALD ONSLOW (*Biochem. J.*, 1920, **14**, 535—540. Compare A., 1919, i, 361).—Solutions of certain compounds, such as catechol, which contain the *o*-dihydroxy-structure, tend to undergo autoxidation when exposed to air with the formation of peroxides. On addition of a solution of peroxydase to these peroxides, an oxydase system is produced which will give the blue colour with guaiacum. The autoxidation of the substances with the *o*-dihydroxy-grouping is accelerated by enzyme extracts of plants which turn brown on injury, and of which the juices turn guaiacum blue without the addition of hydrogen peroxide. Such plants have been found to contain a compound giving the "catechol" reaction, and it is suggested that they also contain an enzyme "oxygenase," which accelerates the production of a peroxide. This enzyme can be separated from peroxydase by fractional precipitation with alcohol, although the converse has not been accomplished.

In the cases which have been investigated, the oxydase system appears to consist of three components: a "catechol" compound from which a peroxide can be formed, oxygenase which catalyses this process, and a peroxydase which decomposes the peroxide with formation of "active" oxygen. J. C. D.

**Oxidising Enzymes. III. The Oxidising Enzymes of Some Common Fruits.** MURIEL WHELDALD ONSLOW (*Biochem. J.*, 1920, **14**, 541—547).—The apple fruit contains the complete oxydase system (see preceding abstract). A large amount of the aromatic compounds of the fruit appears to be present in the form of a catechol tannin, which cannot be activated by the enzyme *in vitro*. The quince, pear, plum, greengage, and damson also contain oxydase. In the case of the banana, both skin and flesh appear to contain peroxydase and oxygenase, but the "catechol" substance is practically absent from the flesh. The fruits of the orange, lemon, and lime contain peroxydase in both the rind and pulp, but no oxygenase or "catechol" substance was found present. The raspberry contains peroxydase, but no oxygenase or catechol substance. J. C. D.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

PART II.

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General and Physical Chemistry.

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**A New Method of Expressing the Formulæ of Line Spectra**

ALFRED LARTIGUE (*Compt. rend.*, 1919, **169**, 914—915).—In place of the general formula  $10^8/\lambda = N_0(1/p^2 - 1/q^2)$  waves per cm., the author proposes to use the formula  $\lambda_m = (4 \times 10^8/N_0) (p/2)^3 [2/p + 1/m - 1/(m+2p)]$  Ångströms, where  $m = q - p$ . W. G.

**Luminous Phenomena Observed in the Neighbourhood of a Plate of Graphite raised to a High Temperature by means of an Electric Current.** G. A. HEMSALECH (*Compt. rend.*, 1919, **169**, 915—918).—A sheet of graphite 0.95 mm. thick had its upper surface covered with a thin layer of carborundum powder, and an electric current was passed through it. As the temperature of the plate increased, when it became incandescent, yellow vapours appeared above the plate and were carried upwards by the air convection currents. When the temperature of the plate reached 2500—2700°, the space bounded by the plate and the air convection currents became filled with a luminous vapour which gave a spectrum composed of rays and bands, whilst the yellow vapours became blue and also luminous, and gave a continuous spectrum. When the temperature of the plate reached 3000°, a red fringe appeared on its lower surface and in contact with it, and was formed by the passage of an electric current through the conducting vapours. Its position could be controlled

by means of the magnetic field from a powerful electro-magnet. This red fringe is of electrical origin, and is probably due to a current of electrons, which decompose the molecules and create centres of emission differing from those of the luminous vapour.

W. G.

**The Spectra Emitted by the Red Fringe and the Luminous Vapour in the Neighbourhood of an Incandescent Plate of Graphite.** G. A. HEMSALECH (*Compt. rend.*, 1919, 169, 1034—1036).—It has previously been shown that the luminous

vapour and red fringe obtained when a plate of graphite is raised by an electric current to high temperatures emit discontinuous spectra (preceding abstract). These spectra have now been examined in detail, and the rays which have been detected are given and the influence of a magnetic field on the centres of emission examined. The spectra of bands and rays, obtained under the experimental conditions, owe their origin to two different types of centres of emission: (1) Those created by the action of heat on the carbides of the metals, the spectrum of which is regulated by the temperature of the graphite plate. The centres of emission are not sensibly influenced by a magnetic field. (2) Those produced by the thermo-electric current, the spectrum of which is regulated both thermally and electrically. The centres of emission are, in this case, very sensitive to magnetic forces.

W. G.

**Reduction Spectra, and in particular that of Magnesium and its Compounds.** J. MEUNIER (*Bull. Soc. Chim.*, 1919, [iv], 25, 562—565).—Using the method previously described, by reduction in a hydrogen flame (compare A., 1919, ii, 132) the author

finds in the ultraviolet region the band composed of the rays  $\lambda=3810, 3829, 3833, 3838, 3851, 3858, 3861$ , and another band consisting of the rays  $\lambda=3885, 3912, 3940, 3960, 3980$ . Nine other rays between  $\lambda=3700$  and  $3780$  have been noticed and their wavelengths approximately determined. Of the salts of magnesium, the chloride, oxychloride, sulphate, nitrate, oxide, and carbonate gave the above spectrum. The pyrophosphate is not, apparently, reduced under these conditions and does not give the above spectrum, phenomena of incandescence, corresponding with the continuous spectrum, being produced.

In some cases, the  $\gamma$ -ray in the neighbourhood of  $\lambda=5003$ , and the broad magnesium ray,  $\lambda=4702$ , are obtained.

W. G.

**The X-ray Spectrum of Tungsten.** M. DE BROGLIE (*Compt. rend.*, 1919, 169, 962—965).—Certain observations, as a result of a long series of experiments, are made on the results of Overn and of Siegbahn (A., 1919, ii, 488) on the spectrum of tungsten. Some of the lines mentioned by Overn the author has not found, whilst on the other hand he has observed certain rays not mentioned by Overn.

For the purpose of obtaining weak bands, the author advocates

the use of a metal shutter pierced with a slit and travelling in front of the sensitive plate with a velocity such that, during the rotation of the crystal, the reflected ray passes continuously through the slit.

W. G.

**Relative Brightness of Dark Radiation at the Melting Points of Gold and Palladium.** FR. HOFFMANN and W. MEISSNER (*Ann. Physik*, 1919, [iv], **60**, 201—232).—The relative brightness of the dark radiation at the melting points of gold and palladium has been measured by two different methods: first, by use of an improved hollow radiator constructed on the Lummer-Kurlbaum principle, whereby the melting point was determined inside the radiator by the wire method; secondly, by use of a hollow radiator which was immersed in the molten metal. The measurements of brightness were made with a König-Martens spectrophotometer. The relative brightness at the melting points of gold and palladium is expressed by 81.5 at the wave-length of  $0.6563\mu$ . The palladium used had the same melting point as that used by Day and Sosman in the gas thermometric measurements. Palladium prepared by repeated precipitation of the ammonium double chloride by means of mercury cyanide gave a very constant melting point, and would serve excellently as a fixed point for temperature determinations. Using  $c=14,300$  as the radiation constant and  $1063^\circ$  as the melting point of gold, it is found that  $1557^\circ$  is the melting point of palladium. This value is about  $8^\circ$  higher than Day and Sosman's figure,  $1549.2^\circ$ .

J. F. S.

**The Ozonogenic Power of the Solar Radiation at the Altitude of the Observatory of Mont Blanc.** RAOUL BAYEUX (*Compt. rend.*, 1919, **169**, 957—959).—At an altitude of 4360 metres, the solar radiation does not cause the polymerisation of oxygen to ozone.

W. G.

**The Absorption of Light by Gases.** G. RIBAUD (*Ann. Physique*, 1919, [ix], **12**, 107—226).—A study of the continuous absorption by bromine vapour in the ultraviolet portion of the spectrum, the conditions being varied as much as possible, the temperature range rising to  $620^\circ$ . The observed experimental curves show notable systematic divergences from the theoretical curves based on the electromagnetic theory of absorption, the weakening (*amortissement*), in particular, calculated for the different regions of the curve, not having the same value. The kinetic theory does not apply to the broad, continuous regions of absorption, and the mechanism of the absorption must be sought in the molecule itself. The author is of the opinion that the weakening (*amortissement*) can be explained by the disturbances of the electron in the interior of the molecule. This conception permits of an explanation of the fact that the breadth of the bands goes on increasing from the ultraviolet to the infra-red.

It is shown that Königsberger's law, that the breadth of the



band is proportional to the square root of the temperature, must be rejected.

In the last part of the paper it is shown that the absorption by the rays of bromine vapour is in close accord with a kinetic theory of absorption, and, in this case, the mobile corpuscle containing the electron is, in all probability, the molecule itself. The magneto-optical properties of the vapours of bromine and iodine in the neighbourhood of the absorption rays have been studied, and it is shown that the rotatory phenomenon observed in the neighbourhood of these rays in iodine vapour is due to a very weak Zeeman effect. The smallness of this effect agrees moderately well with the small values observed for the ratio  $e/m$  in the absorption study.

W. G.

**Chemical Actions of Light.** E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 432—436).—When subjected to prolonged exposure to light, ethyl alcohol does not undergo oxidation, but in presence of oxalic acid it is slowly oxidised in the light, yielding carbon dioxide and formic and acetic acids. Under similar conditions, glycerol (8 grams) gives carbon dioxide, together with other oxidation products equivalent, in their reducing action on Fehling's solution, to 0.351 gram of dextrose. When exposed to light in an atmosphere of oxygen and in presence of water, thiophen yields carbon dioxide and formic, oxalic, and sulphuric acids. Similarly, a benzene solution containing benzophenone and dibenzyl gives rise to benzophenonepinacone and *triphenylbenzyl-ethanol* [ $\alpha\alpha\beta\gamma$ -tetraphenylpropyl alcohol],  $\text{OH}\cdot\text{CPh}_2\cdot\text{CHPh}\cdot\text{CH}_2\text{Ph}$ , which crystallises in long needles, m. p.  $165^\circ$ . In the light, benzoquinone and toluene react to form quinol, quinhydrone, and a small proportion of benzaldehyde. Acetone and *isoamyl* alcohol also react under these conditions, the products identified being (1) *isopropyl* alcohol; (2) *dimethylisobutylethylene glycol* [ $\beta\epsilon$ -*dimethylhexane- $\beta\gamma$ -diol*],  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{OH}$ , b. p.  $136$ — $137^\circ/81$  mm.; (3) *diisobutylethylene glycol* [ $\beta\eta$ -*dimethyloctane- $\delta\epsilon$ -diol*],

$\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CHMe}_2$ ,  
m. p.  $92^\circ$ , which is formed in accordance with the equations:  
 $\text{CH}_3\cdot\text{C}(\text{Me})=\text{C}(\text{Me})_2 + \text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH} =$   
 $\text{CHMe}_2\cdot\text{OH} + \text{CHMe}_2\cdot\text{CH}_2\cdot\text{CHO};$

the latter

$+ \text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH} =$

$\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CHMe}_2;$

(4) resinous products not identified.

T. H. P.

**Photochemical Studies. V. Triboluminescence.** JOH. PLOTNIKOW (*Prometheus*, 1919, **30**, 235—236; from *Chem. Zentr.*, 1919, iv, 462—463).—An apparatus is described with which triboluminescence can be excited under constant, comparable conditions. The triboluminiscope consists of a marble cylinder on which a thick glass plate is pressed, the pressure being regulated by two screws. The substance under investigation is placed between the

plate and the cylinder, and, on rotation of the latter, becomes ground at the point of contact. If the substance is triboluminescent, an illuminated band appears which shines continuously if the rotation is uniform. A special type of camera intended for use in photographing the band is also described. If the substances under investigation are hard enough to abrade the apparatus, the latter is formed from an agate cylinder and a quartz plate. For purposes of demonstration, the use of salophen, which gives a pale green triboluminescence, is recommended.

H. W.

### Relationship between the Range and the Life of $\alpha$ -Rays.

F. KIRCHOF (*Zeitsch. physikal. Chem.*, 1919, **93**, 619—622).—It is shown that the range of the  $\alpha$ -ray emitted by all radioactive elements is shorter the greater the life of the atom producing it. On plotting the range against the half-life, three similar curves are obtained, one for each radioactive family. On plotting the logarithms of the range against the logarithms of the half-life, curves are obtained which indicate that with a range, zero, the life is not infinitely large, but has a finite value about  $10^{15}$ — $10^{18}$  years. Applying this result to Ra-G, the author concludes that it is disintegrating at the above-named rate, but that its  $\alpha$ -ray has no penetrating power. It is also deduced that the  $\alpha$ -rays from isotopes have not the same range, but values corresponding with their own family.

J. F. S.

**The Radioactivity of Uranium.** CHARLES STAEBLING (*Compt. rend.*, 1919, **169**, 1036—1039).—The oxides of uranium studied were obtained from different sources after careful purification and subsequent calcination either of uranyl nitrate or ammonium nitrate. The activities of such oxides were followed over the period from January 13th, 1913, to July 18th, 1914, and a further series of measurements were made in November, 1919. All the oxides studied showed a lowering in penetrating activity varying from 1 to 30.7%, and the curves indicate that half the lowering took place in 6.2 months. The lowering was greatest in the case of the green oxides and least with the black oxides. In the case of a blackish-green oxide, which showed a lowering from 5.95 to 4.64; when this oxide was dissolved in nitric acid and the nitrate again calcined, giving the black oxide, the activity rose again to 5.90. If then this oxide was converted into the green oxide by passage through ammonium uranate, it retained its high restored activity. Renewing the surfaces of the disks did not modify the activities observed.

W. G.

**Dependence of the Di-electric Constant of Gases on Temperature.** HANS RIEGGER (*Ann. Physik*, 1919, [iv], **59**, 753—760).—The dielectric constants for air, hydrogen, methane, carbon dioxide, and carbon monoxide have been measured at low temperatures, and a series of pressures (200—760 mm.) by Mandelstam's dynamometer method (*ibid.*, 1910, **33**, 490). The

results are calculated to 760 mm. pressure in each case by the formula  $(\epsilon_1 - 1)/(\epsilon_2 - 1) = \rho_1/\rho_2$ , and the values for  $\epsilon - 1$  found as follows: air ( $-185.5^\circ$ ), 0.001902; hydrogen ( $-191^\circ$ ), 0.000928; methane ( $-154^\circ$ ), 0.00216; carbon dioxide ( $-73^\circ$ ), 0.001392; carbon monoxide ( $-189^\circ$ ), 0.002633. The values are compared in all cases with those at ordinary temperatures ( $16-18.5^\circ$ ) and 760 mm. pressure.

J. F. S.

### The Theory of Electrolytic Ions. XI. The Limiting Values of Molecular Conductivity and their Determination.

RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1919, 108, 81—110).—The limiting value,  $\mu_\infty$ , of electrical conductivity can be calculated from the so-called Ostwald-Bredig rule,  $\mu_\infty = \mu + \Delta$ , where  $\Delta$  varies with the dilution at which  $\mu$  is observed. The values of  $\Delta$  were determined empirically for the sodium salts of different acids and the chlorides of different bases by Bredig, and are given in his tables for dilutions from 32 to 1024. Two formulæ were given by Kohlrausch for calculating  $\mu_\infty$ , (1) for very high dilutions,  $\mu_\infty - \mu = a[S_0]^{\frac{1}{2}}$ , and (2) for less high dilutions,  $\mu_\infty - \mu = b[S_0]^{\frac{1}{2}}$ , in which  $[S_0]$  is the concentration of the salt and  $a$  and  $b$  are constants. A statistical study of the data available for a very large number of organic cations of the ammonium type has now been made with the object of determining which of these formulæ gives the most reliable values of  $\mu_\infty$ . Both graphic and algebraic methods were used in applying the two Kohlrausch formulæ, and the values found for the constants  $a$  and  $b$  were practically the same by both methods. It was found that  $a$  and  $b$  are undoubtedly "universal" constants, since the deviations from the mean value show no relation to the constitution of the ions. The mean values are  $a$ , 91.54;  $b$ , 58.2. The values of  $\Delta$  in the Ostwald-Bredig formula can be calculated from either of the above equations when the constants are known. When compared with the values given by Bredig, those obtained from the first equation show the best agreement, but this is no proof of their superiority. The two equations give slightly different values for  $\mu_\infty$ , but it is impossible to decide which is the more accurate. From the study of the data for a number of inorganic salts, it was similarly impossible to decide between the two formulæ.

E. H. R.

### The Theory of Electrolytic Ions. XII. The Limiting Values of Molecular Conductivity and Kohlrausch's Extrapolation Law.

RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1919, 108, 191—210. Compare preceding abstract).—For the determination of  $\Delta$  from the relation  $\mu_\infty = \mu + \Delta$ , values of  $\Delta$  are given in Bredig's tables for dilutions from 32 to 1024, these values being applicable to all sodium salts of univalent anions and all chlorides of univalent cations. Bredig's values for  $\Delta$  were arrived at empirically, but they can be calculated from Kohlrausch's equation,  $\mu_\infty - \mu = a[S_0]^{\frac{1}{2}}$ . This calculation has been made for a large number of inorganic salts, the conductivities of which have been accurately

determined, and when the values of  $\Delta$  so obtained are compared with those given by Bredig, considerable disagreement is found. It is shown on theoretical grounds that Bredig's rule is unsound; it gives only a rough approximation to the true value of  $\mu_{\infty}$ . A critical examination of Kohlrausch's conductivity measurements of inorganic salts shows that the formula  $\mu_{\infty} - \mu = a[S_0]^{\frac{1}{2}}$  expresses the results with a high degree of precision for dilutions from 10,000 to 100, whilst from 100 to 10 the formula  $\mu_{\infty} - \mu = b[S_0]^{\frac{1}{3}}$  is better. A more general expression is  $\mu_{\infty} - \mu = A[S_0]^n$ , where  $A$  and  $n$  are functions of the dilution. Whilst in the series of salts of univalent organic cations, the constants  $a$  and  $b$  of the above extrapolation formulæ retain the same value throughout the series (see preceding abstract), in the case of the inorganic salts of univalent cations the values of these constants increase with the atomic weight of the cation in a series such as that from lithium nitrate to cæsium nitrate.

E. H. R.

**Conductivity. V. Measurement of the Conductivity of Solutions.** H. I. SCHLESINGER and F. H. READ (*J. Amer. Chem. Soc.*, 1919, **41**, 1727—1732).—It is shown that although the minima obtained in the measurement of the electrical resistance of solutions may be perfectly sharp, nevertheless the results may be incorrect. This difficulty can be overcome by placing the telephone across the ends of the bridge wire and using an air condenser in parallel with the smaller capacity. It is also shown that the "cell-constant" ought to be determined from solutions which cover the whole range of resistance eventually to be measured.

J. F. S.

**Equilibria Across a Copper Ferrocyanide and an Amyl Alcohol Membrane.** FREDERICK GEORGE DONNAN and WILLIAM EDWARD GARNER (*T.*, 1919, **115**, 1313—1328).

**The Action Exerted by Antagonistic Electrolytes on the Electrical Resistance and Permeability of Emulsion Membranes.** G. H. A. CLOWES (*Proc. Soc. Expt. Biol. Med.*, 1918, **15**, 108—111).—The author brings forward various experimental data derived from electrical conductivity and permeability experiments with artificial emulsion membranes in support of his contention that variations in the permeability of the protoplasmic membrane are attributable to the action of electrolytes and metabolic products on delicately balanced interfacial soap films and emulsion systems and that proteins play no part in the valve-like mechanism controlling permeability other than to afford a supporting filamentous or mesh-like structure. In support of this it is further pointed out that when blood plasma is clotted by the addition of calcium chloride no considerable change in electrical resistance is noted, whilst in the transformation of an emulsion of oil in water into one of water in oil by shaking with calcium chloride the resistance suddenly rises to an enormous extent at the critical point at which oil becomes the continuous or external phase. This all fits in with the well known fact that alkalis, salts of sodium, potassium, etc.,

promote the permeability of tissues whilst salts of calcium, magnesium, and other bi- and ter-valent cations exert the reverse effect, also with the high potassium content and low calcium content of rapidly growing tumours and the reverse relation in slow-growing or stationary tumours.

CHEMICAL ABSTRACTS.

**Phenomenon after Anodic Polarisation. I.** A. SMITS, G. L. C. LA BASTIDE, and J. A. VAN DEN ANDEL (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 82—88).—When the metals iron, nickel, and chromium are anodically polarised in solutions of their salts, using a current density of a definite value, and the potential measured after the polarising current has been broken, it is found that the potential passes through a minimum and then rises to the value before polarisation. Similar experiments with copper and silver did not produce the same effect, so that it appears this phenomenon is only shown in solutions where ions of two stages of oxidation exist or may exist. To test this point the experiment was repeated with iron, using a solution of ferrous chloride, which had been freshly boiled with iron powder, an atmosphere of hydrogen being used. The results show that the minimum potential is no longer observed, and that qualitatively, at least, iron behaves like copper and silver.

J. F. S.

**Potentials of the Zinc and Cadmium Electrodes.** W. GRENVILLE HORSCH (*J. Amer. Chem. Soc.*, 1919, **41**, 1787—1800).—The *E.M.F.* of the following cells has been determined at 25°:  $\text{Zn}|\text{ZnCl}_2|\text{AgCl}|\text{Ag}$ ;  $\text{Cd}(\text{amalgam})|\text{CdCl}_2|\text{AgCl}|\text{Ag}$ ;  $\text{Cd}(\text{amalgam})|\text{CdCl}_2|\text{Cd}$ ; and  $\text{H}_2|\text{HCl}(0.01N)|\text{AgCl}|\text{Ag}$ . In the first cell the concentrations of zinc chloride solution varied from 0.0003*M* to 0.01*M*; in the second the concentration of cadmium chloride varied from 0.0001*M* to 6.61*M* (saturated). The normal electrode potentials of zinc and cadmium were found to be  $0.758 \pm 0.002$  volt and  $0.3992 \pm 0.0010$  volt respectively, the normal hydrogen electrode being taken as zero. The free energy of dilution of zinc chloride and cadmium chloride solution was calculated, and the following values obtained:

$c_1$ .	$c_2$ .	$F(\text{CdCl}_2)$ .	$F(\text{ZnCl}_2)$ .
0.1 <i>M</i>	0.01 <i>M</i>	1306 cal.	—
0.01 <i>M</i>	0.001 <i>M</i>	1615 cal.	1719 cal.
0.005 <i>M</i>	0.0005 <i>M</i>	1705 cal.	1858 cal.

J. F. S.

**The Effect of Amalgamation on the Single Potential of Aluminium.** LOUIS KAHLBERG and JOHN A. MONTGOMERY (*Trans. Amer. Electrochem. Soc.*, **36**, 12 pp.).—The single potential of aluminium was measured in a  $\frac{1}{2}$ *M*-solution of aluminium chloride at the ordinary temperature. The highest value obtained with unamalgamated aluminium was 0.32 volt, and with amalgamated aluminium, 1.00 volt. The mercury removes the coat of resistant oxide. In the first few seconds after immersion the value

1.09 decreases rapidly to 1.04—1.07, owing to formation of oxide over the amalgam. It was shown that the potential measured is actually that of the aluminium, and not that of an aluminium amalgam.

CHEMICAL ABSTRACTS.

**The Potential Necessary for the Electrolysis of Solutions of Iron.** W. ALBERT NOYES, Jun. (*Compt. rend.*, 1919, 164, 971—973).—The minimum potential necessary for the electrolysis of a solution of a ferrous salt between electrodes of electrolytic iron is 0.66 volt at 20°; this value diminishes 0.007 volt for each degree rise in temperature up to 110° when it attains a minimum, and rises again with further rise in temperature.

W. G.

**Electrical Endosmosis of Molten Sodium Chloride in Carbon.** WA. OSTWALD (*Kolloid Zeitsch.*, 1919, 25, 115—116).—When molten sodium chloride is electrolysed between carbon electrodes there is scarcely any evolution of chlorine or formation of sodium unless special conditions are established, but the negative electrode increases in volume and is partly destroyed. On cooling and treating with water the electrode falls to powder, whereas the positive electrode is unaffected either during the electrolysis or on treatment with water. The behaviour is due to the cataphoresis of the molten sodium chloride.

J. F. S.

**Heusler's Alloys.** O. VON AUWERS (*Zeitsch. anorg. Chem.*, 1919, 108, 49—69).—The opinion was expressed by Heusler that the alloys of the aluminium-manganese bronze series owe their ferromagnetic properties to a compound of the form  $(AlM_3)_x$ , where  $M_3$  represents an isomorphous mixture of manganese and copper. Whether the magnetism is to be attributed to simple molecules  $AlM_3$ , to complexes, or to a particular crystal lattice remained obscure. The phenomena attending the so-called ageing of these alloys have an important bearing on the constitution of their ferromagnetic constituent. The cast alloys have weak magnetic properties, and have to undergo the ageing process, that is, prolonged heat treatment at temperatures between 100° and 300°, to develop their full magnetic power. One effect of this treatment is to raise the magnetic transition temperature along a curve similar to a magnetisation curve. When magnetisation is plotted against time of ageing for different field strengths, a series of curves is obtained, of which those for lower field strengths show a sharp maximum with a subsequent fall to a constant magnetisation. In the curves for high field strengths the maximum is flattened out and the corresponding point is followed by a gradual rise in magnetisation as the time of ageing increases. The ageing process appears to involve two superimposed molecular changes. The author considers that at the magnetic transition point the magnetic particles become dissociated. On quenching from about 600° the alloy contains very few magnetic molecules. By slow cooling or by the ageing process the particles again become associated and the magnetisation and coercive force

both increase. With low field strengths the coercive force, that is, the intermolecular force, predominates over the magnetising force, and this explains the maximum in the above-mentioned curves. The highest point of the magnetisation curve is reached when the coercive force is a maximum, that is, when the maximum number of magnetic particles are present. The coercive force depends on the temperature of ageing, and reaches a maximum with temperatures from  $190^{\circ}$  to  $260^{\circ}$ . Above this temperature, it falls off rapidly, presumably because the dissociation of the particles has then commenced.

E. H. R.

**Some Fusion Curves, the Condition Diagram of Resorcinol and the Condition Diagrams of some Cryohydrates.**

WALTER DENECKE (*Zeitsch. anorg. Chem.*, 1919, **108**, 1—43).—The pressure-temperature fusion curves of betol, triphenylmethane, erythritol, guaiacol, salol, and benzoic anhydride, all substances of low crystallisation velocity, have been determined experimentally by Tamman's method, which consists in heating a quantity of the substance under pressure and plotting the temperature-pressure curve. When fusion commences, the curve changes direction owing to a rapid increase in pressure, and the ordinates of the point at which the change of direction starts give the temperature of the melting point and the corresponding pressure. From a number of such observations at different pressures the fusion curve is plotted. The apparatus used was that described by Tamman (*Kristallisieren und Schmelzen*, 1903, 195). In each case the curve can be represented by an equation of the form  $t = t_{p=1\text{Kg}} + ap - bp^2$ , in which  $a$  and  $b$  are constants and  $p$  is the pressure at the fusion point  $t$ . All the curves are smooth, and show no evidence of polymorphism in the substances examined, although betol, triphenylmethane, and erythritol are all known in two or more crystalline modifications.

The same experimental method was applied to the study of the transition between the two forms of resorcinol. The transition of pure resorcinol is extremely slow, but is accelerated by the addition of xylene. In presence of xylene, as the temperature is raised, the pressure begins to fall when the transition commences, the fall being most marked with 1% of xylene. The more xylene there is present, the lower the temperature at which the transition begins. Increasing pressure lowers the transition temperature, but also lowers the transition velocity.

To investigate the separation of different forms of ice from cryohydrate solutions, such solutions of sodium chloride, potassium chloride, ammonium chloride, sucrose and magnesium bromide were studied by cooling under pressures up to 3000 kilos. per sq. cm. down to about  $-70^{\circ}$  and plotting the temperature-pressure curves. The regions of the equilibrium diagram of water in which the ice forms I, II, and III' are stable were thus included. In the ice I field, this form generally separated, but once, from a sodium chloride cryohydrate solution, a form was obtained which appeared to be a less stable form of ice I, and twice, from a magnesium

bromide solution, a more stable form of this group separated. At pressures above 2400 kilos. ice III' was always obtained from sodium chloride solutions, although this is the ice II region. From potassium chloride solutions sometimes ice II and sometimes ice III' was obtained, and from ammonium chloride generally ice V. From sucrose solution ice III' usually separated, but on one occasion a denser form, probably the most stable form of ice II, was observed. When ice I first separated and the pressure was raised subsequently, ice III' was formed, except in the case of magnesium bromide, where the pressure was raised to 3000 kilos. without inducing transition into a denser form of ice. The position of the transition curve of forms I and III' is not changed through the presence of the salts. The salts are therefore not appreciably soluble in these forms of ice.

E. H. R.

### Vapour Pressures of Mercury in the Range 120—250°.

ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1919, **41**, 1783—1787).—A method is described for the measurement of low vapour pressures, involving the use of two McLeod gauges, hot and cold respectively. The method has been used to determine the vapour pressure of mercury at 121.8°, 150.0°, and 191.5°. The following values are found in mm. of mercury: 121.8°, 0.829 mm.; 150.0°, 2.802 mm.; and 191.5°, 13.02 mm. It is shown that the equation connecting vapour pressure and temperature over the temperature range 250—453° (A., 1910, ii, 1037) may be employed without modification of its constants over the range 120—250°.

J. F. S.

### Rectification by Adiabatic Condensation without Expansion.

E. CHENARD (*Bull. Soc. chim.*, 1919, [iv], **25**, 546—552).—As a result of a series of distillations of alcohol-water mixtures through a special apparatus designed (1) to remove from the vapour any liquid transported in the vesicular state, (2) to effect a preliminary partial condensation of the vapour and collection of the condensed portion, it is shown that the law of correspondence between the strengths of liquids and vapours in contact, in a rational process of condensation, is almost identical with the law of fractionation by vaporisation. The process of enrichment of the vapour by means of partial condensation is capable of being very useful and also very simple in its working. Starting with a vapour containing 35% of alcohol, it was found possible by fragmentary condensation, in six stages, of about 54% of the initial weight, to obtain a vapour containing 64% of alcohol. At the same time, the six fractions would, on boiling, give vapours richer than the initial vapour.

W. G.

**Distillation in a High Vacuum.** J. HOUBEN (*Ber.*, 1919, **52**, [B], 1460—1462).—The principle of the method has already been described by Erdmann (A., 1904, ii, 20). A high vacuum is attained by means of an ordinary water pump through filling the



apparatus with carbon dioxide and condensing it in a suitable receiver by liquid air. The new improvement consists in letting the carbon dioxide enter in a continual stream through a fine capillary below the liquid, so as to prevent uneven boiling. A pressure of 0.12 mm. is easily maintained. J. C. W.

**Comparative Investigation of the Efficiency of Still-heads of Various Types.** J. FRIEDRICHS (*Zeitsch. angew. Chem.*, 1919, **32**, 340—344).—In order to test the efficiency of different types of still-head, a mixture of equal quantities of benzene and toluene was distilled at a constant speed, which was controlled by means of a vapour pressure regulator between the still-head and the condenser. The temperature within the still-head and the volumes of distillate were taken at regular intervals, and the results are given in tabular form. It was found that still-heads containing glass beads or fragments were the most effective, whilst for the distillation of larger quantities of liquid the use of a long tube, as in Hempel's apparatus, is best. Winssinger's modification of Hempel's still-head gives good results with liquids boiling below 100°, whilst a modification of Plücker's apparatus combines the advantages of Winssinger's dephlegmator and Ekenberg's rectifying apparatus. In the case of small amounts of liquids, Linne-mann's apparatus gives the best results. [See also *J. Soc. Chem. Ind.*, 1919, 964A.] C. A. M.

**Heat of Hydration of Gaseous Ions.** K. FAJANS (*Ber. deut. physikal. Ges.*, 1919, **21**, 549—558).—The heat of solution of a salt in water is regarded as made up of two quantities, (i) the heat absorption necessary for complete dissociation of the salt into gaseous ions, and (ii) the heat developed in the solution of these ions in water. The latter quantity is termed the heat of hydration of gaseous ions. From a knowledge of  $L$ , the heat of solution of a binary salt, and  $U$ , the total energy change, the author shows that the heats of hydration of the gaseous ions may be calculated. Employing this method, the following values, in kilogram cal. per gram-ion, are calculated:  $H^+$ , 362;  $Li^+$ , 210;  $Na^+$ , 203;  $K^+$ , 182;  $Rb^+$ , 173;  $Cs^+$ , 174;  $Tl^+$ , 182;  $Ca^{++}$ , 475;  $Cl^-$ , -23;  $Br^-$ , -32;  $I^-$ , -43. The values are claimed to be accurate within 6 units in the case of cations and 10 units in the case of anions. J. F. S.

**Heat of Ionisation and Chemical Constitution.** E. OLIVERI-MANDALÀ (*Gazzetta*, 1919, **49**, ii, 176—180).—With a few exceptions, weak electrolytes exhibit heats of ionisation differing little from a mean value of 500 cal., and attempts have been made to explain the exceptional values by means of the chemical constitution of the electrolytes concerned. Thus, according to Bauer (*A.*, 1897, ii, 546), the magnitude of the heat of ionisation may indicate the union of the hydrogen of an electrolyte to a nitrogen rather than to an oxygen atom, whilst Hantzsch employs it to diagnose

the presence in solution of a pseudo-acid, and Jones considers that anomalous heats of ionisation support his hydrate theory. Further, the high heats of ionisation shown by water and hydrofluoric acid have been explained as the result of a process of depolymerisation.

The author points out that the heat of ionisation, calculated from the heat of dissociation, depends on the other constants of the equilibria existing in solution and on the thermal effects of these equilibria, so that the magnitude of the heat of ionisation of a substance cannot serve as a physico-chemical means of investigating either intramolecular changes of electrolytes in solution or transformations of other character. The particular cases of a pseudo-acid and of hydrofluoric acid are considered, and an equation identical in form with, but different in signification from, that found by Lunden in the case of ammonia is derived (compare A., 1916, ii, 367).  
T. H. P.

**Differences in the Heats of Combustion and in Other Properties of Isomeric Forms of Compounds of the Type Tartaric Acid-Mesotartaric Acid.** E. BERNER (*Tidskrift Kemi*, 1919, **16**, 97—110, 118—128).—The differences in the heat of combustion, density, solubility, and sublimation point were ascertained for the isomeric forms of tartaric acid, phenylglyceric acid, and hydrobenzoin. For the heat of combustion, the units in the following are kilo. cal. per gram-mol. The methyl ester was used in place of tartaric acid. Tartaric acid in the *meso*-form gave 623.2 Cal., in the *d*-form 621.8 Cal. Correcting for the difference in the heat of solution, the difference between these two is 2.6 Cal. Corresponding stereoisomeric forms of phenylglyceric acid (m. p.'s 122° and 141° respectively) gave 1011.2 and 1004.2 Cal., a difference of 5.4 Cal. after correcting for the heat of solution. In hydrobenzoin and *isohydrobenzoin* the relations are reversed, the stereoisomeride corresponding with *i*-tartaric acid giving a smaller heat of combustion (1723.2 Cal.) than the other isomeride (1728.0 Cal.). The difference after correcting for the heat of solution is 4.5 Cal. *r*-Tartaric acid gave 0.5 Cal. more heat than did the *d*-isomeride. The author concedes that this may have been an experimental error, but cites Ossipoff (*Compt. rend.*, 1889, **109**, 475), who also noted a difference in the heats of combustion of these two isomerides, namely, 619.5 and 618.5 Cal. Attention is directed to the fact that the first four substances mentioned above are derived from the following acids, with heats of combustion as indicated: maleic (329.6), fumaric (320.7), *allocinnamic* (1047.6), and *cinnamic* (1042.3 Cal.), respectively, and that in the transformation the relative rank as to energy is not altered. In isomeric forms greater solubility and lower m. p., sublimation point, density, and molecular volume in solution are associated with the isomerides of higher heats of combustion. The tartaric acids are an exception to this rule, as are also maleic and fumaric acids, from which the tartaric acid isomerides may be derived.

**The Benzene [Formula] Problem. II.** A. VON WEINBERG (*Ber.*, 1919, 52, [B], 1501—1508).—From the data for the heats of combustion of various hydrocarbons, a discussion of the kinetics of benzene and related compounds is developed.

In the first place, it is shown that the heat of combustion of a saturated hydrocarbon,  $C_nH_m$ , can be expressed very nearly by the term  $96n + 30m$  Cal., that is, each carbon and each hydrogen atom contributes a constant quantity. This is developed from two series of data. (1) Let  $x$  = the contribution of the carbon atom, and  $y$  that of the hydrogen. Then, in the case of ethane,  $2x + 6y = 370.9$ , and in the case of propane,  $3x + 8y = 526.7$ , whence  $x = 96.5$  and  $y = 29.65$ . (2) The increment for the  $\cdot CH_3$  group is known to be 156 Cal., and the average heat of combustion of the isomeric octanes is 1299.9 Cal. (Richard and Jesse, A., 1910, ii, 269). To the latter value should be added the latent heat of vaporisation, which is 8.09 Cal. Then  $x + 2y = 156$  and  $8(x + 2y) + 2y = 1308$ , whence  $x = 96$  and  $y = 30$ . Two consequences follow from this additivity. First, the energy of the rupture of a C·H linking must be the same as that of a C·C bond, and, secondly, the heat of combustion of a carbon atom in gaseous carbon must be the same as that of a carbon atom in a simple hydrocarbon vapour. Now it is quite remarkable that the above value, 96, is very nearly the same as the heat of combustion of solid carbon, from which it appears that in the vaporisation of carbon there is very little force of cohesion to overcome. This is in accordance with the view that carbon is mono-atomic in the diamond, as revealed by a study of the space-lattice and diminution of the specific heat at low temperatures.

The heat of dissociation of the C·H or C·C linking can be calculated as follows. The heat of combustion for one H in hydrocarbons is 30, but for two H atoms in hydrogen gas it is not 60, but 67.5, that is, the heat of dissociation of the C·H bond is less than that of H·H by 7.5. The value used by Nernst for the heat of dissociation of hydrogen is 100 Cal., from which it follows that the required quantity is 92.5 Cal.

The additional energy of the molecule due to one or more double linkings may be calculated by subtracting the value for the term  $96n + 30m$  from the heat of combustion. From the values for ethylene, propylene, and hexylene, it appears that the increment due to the single ethylene linking is equivalent to about 30 Cal. For  $\Delta^{2,5}$ -hexadiene, however, it is only 16.3, instead of twice 30, and for  $\epsilon$ -methyl- $\Delta^{2,5}$ -hexadiene it is only 20.8. This is due to the fact that the oscillations set up by one double bond interfere with and restrict those of the other. The case of the conjugated linkings is most interesting, for this really represents the energy of vibration of three pairs. Now if benzene has three conjugated double bonds, the energy of six oscillating pairs will have to be reckoned, that is,  $2 \times 16.3 = 32.6$  Cal. Actually, the additional energy given out by benzene, above that calculated from the term  $6 \times 96 + 6 \times 30$ , is 32.7 Cal. if Roth's value for the heat of combus-

tion is correct (A., 1915, ii, 146), or 30.3 if Richards and Barry's number is accepted (*ibid.*, 421). The oscillation energy of each carbon atom in benzene is therefore 5.4 or 5.05 Cal., that is, about one-third of the energy of an ethylenic carbon atom. This agrees with the fact that the oscillation frequencies are slower in benzene and approach those of the visible spectrum. From the data available for naphthalene and anthracene, it appears that the average oscillation energy for one carbon atom is again about 5 Cal. Formulæ are given with which it is possible to discuss the amplitudes and frequencies of the oscillations of the  $\alpha$ - and  $\beta$ -carbon atoms in these compounds.

The excess energy in the case of *cyclohexane*, that is, the energy due to ring formation, is 8.2 Cal. This rises to 23.6 when one ethylene linking is also present (*cyclohexene*), to 38.6 when two are present (*cyclohexadiene*), but is 32.7 in the case of benzene.

J. C. W.

**New Gas Pyknometer.** K. KLING and L. SUCHOWEAK (*Metan*, 1917, 1, 37—42; from *Chem. Zentr.*, 1919, iv, 437—439).—The authors describe a new form of gas pyknometer suitable for use with small quantities of gas and for the estimation of density without using a current of gas or a pump. The principle of the apparatus depends on the observation that carefully purified and dry mercury flows quantitatively from the well-cleaned apparatus. A single filling of the pyknometer by mercury suction leaves the vessel quantitatively filled with the gas. A further feature is the complete absence of stopcocks. The apparatus is very fully illustrated in the original.

H. W.

**Table for the Correction of Volumes of Gases.** W. OSTWALD (*Zeitsch. angew. Chem.*, 1919, 32, 359—360).—A calculation diagram for the correction of gas volumes to normal temperature and pressure, including correction for the tension of aqueous vapour, may be constructed by plotting the values for barometer readings and the ascertained correction factors on two parallel logarithmic scales, joining the respective points on these scales by a straight edge and marking points between them to represent the corresponding temperatures. The temperature scale thus plotted includes the aqueous vapour correction, and will be found to take the form of a straight line parallel to the other two. The barometric and temperature scales can then be used for finding the corresponding correction factor without calculation, and the multiplication of the observed volume by this factor to obtain the corrected volume may be performed graphically, in the same manner by constructing two other logarithmic volume scales on the same diagram.

J. F. B.

**Molecular Volumes.** W. HERZ (*Zeitsch. anorg. Chem.*, 1919, 108, 226—230).—For a number of homologous series of organic compounds, the author has compared the "true" molecular volumes given by the expression  $V = D - 1/D + 2.M/d$ , where  $D$  is the

dielectric constant and  $d$  the density, with the molecular volume at absolute zero,  $V_0$  (A., 1919, ii, 220). In general, both  $V$  and  $V_0$  increase with the molecular weight, although acetic acid shows an abnormally high value for  $V$  in the series of homologous acids. The molecular volumes at absolute zero are greater than the true molecular volumes, and the difference increases with the molecular weight. In the benzene series, the ratio  $V/V_0$  is a constant, and the same is true in the paraffin series from hexane to decane. In the fatty acids, the alkyl formates, and alkyl acetates the ratio decreases as the series is ascended, but it approximates to a constant value in the higher members of each series. In the early members of these three series, the difference between the two molecular volumes is very small, indicating that the substances have a very compact structure. In the alcohol series, from methyl to amyl alcohol, the true molecular volume appears to be actually greater than the molecular volume at absolute zero. The abnormality becomes smaller with increasing molecular weight, and disappears beyond amyl alcohol. It is probably due to association in the alcohols, as a similar abnormality is found in the case of formic acid.

E. H. R.

**Molecular Volumes of Liquid Organic Compounds.** HUGO KAUFFMANN (*Zeitsch. Elektrochem.*, 1919, 25, 343—351).—The author has examined the molecular volumes of a large number of organic compounds, using the experimental data of Lossens (A., 1890, 323) for the purpose. It is shown that the molecular volume at the boiling point is not suitable for the investigation of regularities or for the calculation of atomic volumes. The molecular volume at a given temperature brings important regularities to light which run parallel with other physical properties. The density in homologous series of organic compounds approaches limiting values characteristic for each temperature; thus, at 0°  $D=0.8752$ ; at 20°  $D=0.8616$  as a limit. If the density of the first member of an homologous series is smaller than the limit, then the density in that series increases with increasing molecular weight, but should the density of the first member be larger than the limit then the density falls with increasing molecular weight in that series. The author recognises "Accumulation phenomena." This is the name applied to the combination of several groups or atoms with a given atom. Accumulation increases the molecular volume, and this mainly in the third and fourth stage. This is equally true for mixed and similar accumulation. Atoms or groups which bring about exclusively large increases in the molecular volume are termed *Eurogens*, and the accumulation phenomenon itself is termed *Eurogenism*. Carbethoxyl-, chlorine, nitro- and cyanogen groups are strong eurogens. The strength of the eurogens named increases in the order given; and other carbonyl-containing groups are stronger than the carbethoxyl group. The ethoxyl and phenyl groups are weaker than the carbethoxyl group, and the  $-CO\cdot O-$  group is a bivalent eugen. Of the alcohol radicles,

only the methyl group has eurogenic properties. This peculiarity of the methyl group has the effect that the second member of every homologous series shows a slight irregularity in the approach to the limiting value. The molecular volume of isomeric aliphatic compounds is controlled largely by the eurogenic character of the methyl group. In substituted derivatives the eurogenic influence of the methyl group is combined with its substitution influence. The difference between the molecular volumes of isomerides is a measure of the eurogenism. In accumulation of the second stage the methyl group may lose some of its activity, since methyl groups when they are combined with neighbouring carbon atoms, acting as accumulation centres, reduce the molecular volume. A similar state of affairs is shown to exist in silicon compounds where the silicon atom is acting as the accumulation centre.

J. F. S.

**A Thermodynamic Proof.** ARRIGO MAZZUCHELLI (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 47—51).—Lewis [*“System of Physical Chemistry”* (2nd Ed.); II, 140] directs attention to the divergent results attained by two proofs, both apparently unobjectionable, of the relation between pressure and equilibrium constant in dilute solutions. One of these proofs is due to Planck, who arrives at formula 220 of his *“Thermodynamik”* (3rd Ed.), and the other to Rice (*Trans. Faraday Soc.*, 1917, **12**, 318), who derives the formula  $d/dP \log K = (V_1 - V_2)/RT$ , where  $K$  is the equilibrium constant (constant of formation of the final system referred to concentration by volume) and  $V_2 - V_1$  the variation in volume due to the integral transformation of the initial system into the final one. The author introduces certain modifications into Rice's system and shows that Rice's cycle then leads to Planck's formula, although he does not claim to have proved that such modifications are justified.

In the cases which up to the present have been subjected to experiment, a compression, besides altering the equilibrium constant in the sense favouring the system with a less total volume, that is, in accordance with the Le Chatelier-van't Hoff principle, also causes a certain increase in the concentration by volume, owing to the compressibility of the solution. Such increase in concentration, although without direct influence on the equilibrium constant, yet favours as a rule the system with the less number of molecules, of which it increases the relative quantity; in the experimental measurements, such increase figures, therefore, as a further variation of the equilibrium constant, and it should be taken into account by any rigorous theoretical formula.

T. H. P.

**Surface Tension and its Relationship to Other Properties of Liquids.** W. HERZ (*Zeitsch. physikal. Chem.*, 1919, **93**, 607—612).—A theoretical paper in which the author examines the values of the surface tension, molecular surface energy, the temperature-coefficient of the molecular surface energy, and the molecular association of a number of organic compounds in their relations to the number of carbon atoms in the molecule. It is shown

that in homologous series the surface tension decreases with increasing number of carbon atoms, whilst the molecular surface energy becomes larger. The temperature-coefficient of the molecular surface energy increases in homologous series at the same temperature with the number of carbon atoms. From this it is deduced that the tendency to association decreases as the number of carbon atoms increases. Richard's rule that the compressibility is inversely proportional to the surface tension is examined in a large number of cases and confirmed. The compressibility is larger the fewer the molecules in unit volume, that is, the larger the molecular diameter.

J. F. S.

**The Technique of the Estimation of the Viscosity of Organic Colloids.** E. ROTHLIN (*Biochem. Zeitsch.*, 1919, **98**, 34—92).—The superiority of the "capillary" methods over the "damping" methods in the estimation of the viscosity of fluids is discussed. The author examined the viscosity of various emulsoids under different pressures by means of Hess's viscometer (capillary principle). Emulsoids, like gum arabic, soluble starch,  $\beta$ -gelatin, and casein, have been found to obey Poiseuille's law. Others like gelatin, egg-white, insoluble starch, agar, and soap have shown a deviation from the above-mentioned law as the pressure was diminished. In the case of one of these colloids, namely, gelatin, higher temperatures, the addition of hydrochloric acid, sodium hydroxide, sodium chloride of suitable concentrations as well as alcohol prevented this deviation. Two pressure regions in the viscosity of these emulsoids could be differentiated, the "upper" region, in which the colloids practically obeyed Poiseuille's law, and the "lower" region, in which they deviated from it. This deviation under low pressure the author attributes to the cohesive forces of the particles. The importance of the pressure factor and the dimensions of the capillaries in the estimation of the viscosity of fluids is pointed out. Hess's viscometer fulfils these requirements.

S. S. Z.

**Influence of the Red Blood Corpuscles on the Internal Friction of Blood.** KARL BECK (*Kolloid Zeitsch.*, 1919, **25**, 109—110).—The viscosity of human blood has been measured with the object of ascertaining the relationship between this value and also of testing the Einstein relationship,  $K' = K(1 + 2.57)$  (*Ann. Physik*, 1906, **19**, 289; 1911, **34**, 591). It is shown that the  $\alpha$  value depends on the number of suspended particles in the sense that at small concentrations the influence on the viscosity is smaller, and at high concentrations larger, than would be the case with a constant value of  $\alpha$  (2.5). This is in keeping with previous results obtained for emulsions of oil (*A.*, 1904, ii, 646; 1907, ii, 232). It follows, therefore, that the influence of a non-rigid particle on the viscosity cannot be determined either by Einstein's formula or by any simple application of the mixture rule.

J. F. S.

**Wo. Ostwald's Rule Connecting Colour and Degree of Dispersion.** E. WEDEKIND and H. RHEINBOLDT (*Ber.*, 1919, 52, [B], 1794).—A note to remove a possible misconception of the authors' views on Ostwald's theories (*A.*, 1919, ii, 270).

J. C. W.

**The Effect of Salts on the Vapour Pressure and Degree of Dissociation of Acetic Acid in Solution. An Experimental Refutation of the Hypothesis that Neutral Salts Increase the Dissociation Constants of Weak Acids and Bases.** JAMES WILLIAM MCBAIN and JAMES KAM (*T.*, 1919, 115, 1332—1346).

**Resolution of the Acid Salts of Dicarboxylic Acids into the Free Acids and the Normal Salts.** JOH. PINNOW (*Ber.*, 1919, 52, [B], 1662—1667).—The method of estimating the first and second dissociation constants of dibasic organic acids proposed by McCoy (*A.*, 1908, ii, 466, 467), namely, by extracting solutions of the acid salts with ether and determining the partition-coefficient of the acid, has been tested by Dieckmann and Hardt (*A.*, 1919, ii, 326), who found that the ratio  $k_1:k_2$  is not always independent of the concentration, as it should be. They consequently formed the opinion that there are sources of error inherent in the method itself. Some of these are now discussed.

In the first place, the determination of the partition coefficient for the acid will be influenced by association and ionisation. As the solution becomes more dilute, the associated molecules become fewer and the rate of extraction rises to a constant value (see *A.*, 1915, ii, 679). Then it begins to fall unless some sulphuric acid is added to prevent ionisation. Another factor is the "salting out" effect of the normal and acid salts, which is, of course, less in dilute solutions than in concentrated ones. The question whether any of the metallic salt is extracted by ether in the Partheil-Rose apparatus used in these investigations has been tested in the case of sodium and potassium hydrogen oxalates and potassium tetroxalate but the quantity is found to be quite negligible.

The relationship between free acid ( $f$ ), acid salt ( $m$ ), and normal salt ( $d$ ), as expressed in the term  $m^2/f \cdot d$ , is independent of the nature of the alkali in the case of succinic acid.

J. C. W.

**Structure of the Capillary Layer. III.** G. BAKKER (*Zeitsch. physikal. Chem.*, 1919, 93, 570—584. Compare *A.*, 1915, ii, 614; 1916, ii, 553).—The capillary layer is regarded as a film which has been formed by and between the liquid and gaseous phases without changing the total mass of these two phases. If  $n$  is the total number of molecular layers of gas and liquid which go to form the capillary layer consisting of  $R$  new layers, then  $R = qn$ , where  $q$  is a characteristic constant. Making use of the Laplace formula for molecular pressure,  $Q = a/2(\sqrt[3]{\rho_1} + \sqrt[3]{\rho_2}) \cdot \sqrt[3]{M/N} \cdot (\rho_1 - \rho_2)^2/H$  or  $\frac{1}{2}(\sqrt[3]{\rho_1} + \sqrt[3]{\rho_2}) \cdot \sqrt[3]{M/N} \cdot r_1(\rho_1 - \rho_2)/1 - T/a \cdot (d\sigma/dt)$ , in which  $a$  is



the Laplace constant,  $\rho_1$  the density of the liquid,  $\rho_2$  the density of the vapour,  $M$  the molecular weight,  $N$  the Avogadro number,  $H$  the surface tension,  $r_i$  the internal heat of vaporisation. Both formulæ are identical, since the equation  $p = Tf(v) - a/v^2$  has been used in developing them. The equation for the number of layers in the capillary layer therefore becomes

$$R = 1 + Q/q + \sqrt{2Q/q + Q^2/q^2}.$$

If, however, the more exact formula of Clausius is used for the molecular pressure,  $Q = \frac{1}{2}(\sqrt[3]{\rho_1} + \sqrt[3]{\rho_2})\sqrt{M/N} \cdot r_i(\rho_1 - \rho_2)/(1 - T/a \cdot da/dt) \cdot (1 + \beta\rho_1)(1 + \beta\rho_2)$ . By means of these formulæ, the number of layers in the capillary layer, the thickness of the layer, and the number of molecular layers of vapour and liquid going in its formation have been calculated for carbon dioxide, benzene, and ethyl ether. The following values are obtained at the temperatures given:

*Carbon Dioxide.*

$t$	$-25^\circ$	$-10^\circ$	$0^\circ$	$10^\circ$	$20^\circ$	$28^\circ$	$30^\circ$
$R$	4.8	5.4	5.4	6.9	8.8	13.3	28
$n$	4.3	5.0	5.1	6.6	8.6	13.2	28
$\zeta$	2.6	2.9	2.9	3.7	4.8	7.2	15 $\mu\mu$

*Benzene.*

$t$	$5.4^\circ$	$50^\circ$	$80^\circ$	$100^\circ$	$150^\circ$	$200^\circ$	$250^\circ$	$275^\circ$	$280^\circ$
$R$	3.8	5.27	5.0	5.23	5.35	5.8	8.3	12.7	17.8
$n$	2.9	4.3	4.2	4.5	4.7	5.4	8.0	12.4	17.7

*Ethyl Ether.*

$t$	$0^\circ$	$20^\circ$	$50^\circ$	$80^\circ$	$120^\circ$	$170^\circ$	$190^\circ$	$193^\circ$
$R$	4.2	5.1	5.1	6.1	7.0	9.6	18.4	24.5
$n$	3.4	4.2	4.4	5.4	6.4	9.3	18.2	24.5

The present results are compared with, and criticised in connexion with, the results published in previous papers (*loc. cit.*).

J. F. S.

**The Molecular Theory of Solution.** SAMUEL CLEMENT BRADFORD (*Phil. Mag.*, 1919, [vi], **38**, 696—705).—The theory of solution is considered from the point of view of the attractions of the solute and solvent particles for themselves and for one another. Whereas on Traube's "cohesion pressure" theory of solution, wherein cohesion pressure signifies the attraction of solute and solvent, the solubilities of organic liquids follow the order of their cohesion pressures, the solubilities of solid substances are in the reverse order. On the basis of the kinetic theory, the electronic theory leads to an expression of the form  $f = M_w^2/r_w^4 - 2M_sM_w/r_{sw}^4 + M_s^2/r_s^4$ , where  $M_w$  and  $M_s$  are respectively the moments of atomic doublets in solute and solvent, and  $r_w$ ,  $r_{sw}$ , and  $r_s$  the respective distances between the centres of two solvent doublets, a solute-solvent doublet, and two solute doublets for the force initially tending to prevent solution.

This relation, combined with that expressing the ratio of the number of molecules in unit volume of the liquid solvent to the number in unit volume of the solid solute, is employed to deduce a number of conclusions relating to solution. Thus, the more a solute increases the surface tension of the solvent, the less its solubility. In the case of solutes which increase the surface tension of the solvent, the order of the compressibilities of their solutions will be the same as that of the solubilities of the respective solutes. Salts have a greater solubility, the larger their respective molecular volumes. It is shown that in accordance with the theory developed, the solubilities of sulphur dioxide, hydrogen sulphide, nitrous oxide, carbon dioxide, carbon monoxide, oxygen, nitrogen, and hydrogen are greater in alcohol than in water, and that, moreover, the difference of solubilities in the two liquids increases as the molecular cohesion of the gas diminishes.

J. S. G. T.

### **Thermochemical Proof of Born's Crystal Lattice Theory.**

K. FAJANS (*Ber. deut. physikal. Ges.*, 1919, **21**, 539—548).—The author has calculated the energy of formation of gaseous ions from the crystalline salt by means of the known experimental values for the heat of solution of calcium chloride, calcium iodide, lithium iodide and chloride. These results are compared with the corresponding values calculated on the basis of Born's cubic atom model theory (A., 1919, ii, 188). It is shown that the two sets of values are in excellent agreement, and that they furnish a confirmation of this theory.

J. F. S.

### **Colloid Synthesis by means of Oscillating Arcs.**

GÖSTA BÖRJESON and THE. SVEDBERG (*Kolloid Zeitsch.*, 1919, **25**, 154—158).—Using capacities in circuit, arcs of various metals have been struck in alcohol when the disintegrated metal forms colloidal solutions. In the experiments with a capacity of  $12.8 \times 10^{-3} MF$  and a current of 1.5 amperes colloidal solutions of antimony, lead, bismuth, zinc, gold, platinum, silver, copper, aluminium, and cadmium have been obtained. By this method the colloidal metal is produced more rapidly than by the earlier Svedberg method, in some cases four times as rapidly. The stability of the sols is fairly great, although a certain amount always separates, but even then the bulk of the metal remains in solution. Gold and platinum are exceptional, being very unstable.

J. F. S.

### **The Effect of Organic Acids and their Amino-compounds on the Hydration of Agar and on a Biocolloid.**

D. T. MACDOUGAL and H. A. SPOEHR (*Proc. Soc. Expt. Biol. Med.*, 1918, **16**, 33—35).—Three groups of substances were selected: (1) succinic acid and its amino-compound, aspartic acid, both of which are dibasic, and its amide, asparagine, which is monobasic; (2) acetic acid and glycine, which are monobasic; (3) propionic acid and alanine, also monobasic, their action on the swelling of sections of agar and a mixture of 8 parts of agar and 2 parts of oat protein being

studied. Equimolecular concentrations of the three organic acids present small divergence of effect on agar and more positive differences in agar-protein. Agar swells more in succinic acid than in its amino-compound, but reverses this relation with the other two acids and their amino-compounds. The agar protein biocolloid showed greater hydration in the amino-acids than in the related organic acids, greater even than in distilled water. Glycine facilitates hydration in all concentrations above 0.01M in both agar and agar-protein, and also in agar-gelatin. The amide, asparagine, induces a maximal hydration, greater even than that possible in agar in distilled water and very high at all concentrations.

CHEMICAL ABSTRACTS.

**Protective Colloids. 2nd Series. Cetraria Islandica as Protecting Colloid. IV. Colloidal Copper.** A. GUTBIER and E. SAUER (*Kolloid Zeitsch.*, 1919, **25**, 145—153. Compare A., 1916, ii, 231, 303).—Extract of Iceland moss has been prepared in three ways: *A*, by extracting the moss with distilled water; *B*, by washing the moss first with dilute potassium carbonate and then extracting with water; *C*, the product *B* is rubbed with distilled water and then stirred with water and dialysed. These three extracts were used as protective colloids in the preparation of colloidal copper solutions from ammoniacal copper sulphate solutions and hydrazine hydrate. The copper sols are so very sensitive that it was possible to test the three extracts as to their protective action. Extract *C* is by far the most efficient, and *B* is far superior to *A*. The sols produced, using 0.1—0.05% of cetraria extract, are fairly stable, but deposit a dark red precipitate in fourteen days, which is reversible. Colloidal copper solutions which by transmitted light are clear red and slightly turbid by reflected light on keeping, deposit fine-grained, irreversible precipitates, but those which are bright red in both lights deposit completely reversible precipitates. The preparation of the solid colloid may be effected by adding  $\frac{1}{2}$ — $\frac{1}{3}$  volume of alcohol. The colloids thus obtainable are not very rich in copper, the limit of absolute reversibility being reached with a copper content of 13.43%.  
J. F. S.

**Relationship between Shrinking and Diffusion Structure in Tanned (Hardened) Gelatin Jellies.** W. MOELLER (*Kolloid Zeitsch.*, 1919, **25**, 101—109).—The structures of hardened jellies produced by shrinking and by the diffusion of solutions into the jellies have been investigated. It is shown that the structures, produced by the diffusion of solutions of sodium hydroxide into gelatin-sodium chloride jellies which have been hardened by formaldehyde, are due to changes in the internal structure of the micellar envelope. The thin, tanned layer attaches itself closely to the underlying coarse structure, and completely follows the direction of the coarser structure. Under tension, shrinkage lines appear in radial directions from the diffusion centre, and concentric ring systems are produced by the contractions of the micellar envelope

Irregularities may be caused by the passage of drops of alkali hydroxide solution through the fine pores of the surface film.

J. F. S.

**Studies in Catalysis. Part XII. Catalytic Criteria and the Radiation Hypothesis.** WILLIAM CUDMORE MCCULLAGH LEWIS (T., 1919, 115, 1360—1366).

**Calculation of the Ammonia Gas Equilibrium.** EDUARD MAURER (*Zeitsch. anorg. Chem.*, 1919, 108, 273—302).—A comparison is made of the results obtained for the nitrogen-hydrogen-ammonia equilibrium at different temperatures and pressures by Haber and Le Rossignol and Jost (A., 1908, ii, 362, 761) respectively. It is concluded that the results of these experimenters are in full agreement, and further that the work of Jost, carried out in Nernst's laboratory, was a sufficient scientific foundation for the technical synthesis of ammonia.

E. H. R.

**The Equilibrium between Carbon, Hydrogen, and Methane.** HUBERT FRANK COWARD and STANLEY PIERCE WILSON (T., 1919, 115, 1380—1387).

**Calculation of the Temperature-coefficient of the Distribution Ratio.** F. H. MACDOUGALL (*J. Amer. Chem. Soc.*, 1919, 41, 1718—1721).—A mathematical paper in which the author derives the temperature-coefficient of the distribution ratio for succinic acid between water and ether. This value has previously been deduced by Forbes and Coolidge (A., 1919, ii, 141), but the present author points out that the mathematical expression is likely to be misleading. The present expression has the form  $dR/dt = 1/\sigma_s[(b_1 + a_1n_2)/(1 - a_1m_2) - R \cdot (\beta_1 + a_1v_2)/(1 - \alpha_1\mu_2)]$ , which is identical with that of Coolidge and Forbes. The Greek letters refer to the ether phase, and the Roman letters to the aqueous phase,  $\sigma_s$  is the mol. fraction of acid in water saturated with ether,  $b_1 = \text{Lim}(ds_1/dt)e_1$ , where  $e_1$  is the mol. fraction of ether in the water layer, saturated with acid but not with ether, and  $s_1$  is the mol. fraction of acid in the water layer saturated with acid but not with ether;  $n_2 = \text{Lim}(de_2/dt)s_1$ ; the meanings of the other symbols follow the same order.

J. F. S.

**Relations between Distribution Ratio, Temperature, and Concentration in System: Water, Ether, Succinic Acid.** G. S. FORBES and A. S. COOLIDGE (*J. Amer. Chem. Soc.*, 1919, 41, 1721. Compare preceding abstract, also A., 1919, ii, 141).—An acknowledgment of Macdougall's paper (*loc. cit.*) and an indication of the method by which a misinterpretation of the previous equation may be avoided.

J. F. S.

**The Propagation of Flame in Complex Gaseous Mixtures. I. Limit Mixtures and the Uniform Movement of Flame in such Mixtures.** WILLIAM PAYMAN (T., 1919, 115, 1436—1445).

**The Propagation of Flame in Complex Gaseous Mixtures. II. The Uniform Movement of Flame in Mixtures of Air with the Paraffin Hydrocarbons.** WILLIAM PAYMAN (T., 1919, 115, 1446—1453).

**The Propagation of Flame in Complex Gaseous Mixtures. III. The Uniform Movement of Flame in Mixtures of Air with Mixtures of Methane, Hydrogen, and Carbon Monoxide, and with Industrial Inflammable Gases.** WILLIAM PAYMAN (T., 1919, 115, 1454—1462).

**The Ignition of Ether-Alcohol-Air and Acetone-Air Mixtures in Contact with Heated Surfaces.** ALBERT GREVILLE WHITE and TUDOR WILLIAMS PRICE (T., 1919, 115, 1462—1505).

**The Diastatic Inversion of Sucrose: Influence of the Products of the Reaction on the Velocity of Hydrolysis.** H. COLIN and (MLLE.) A. CHAUDUN (*Compt. rend.*, 1919, 169, 849—852).—It has been shown previously (compare A., 1919, ii, 327) that the diminution in the velocity of inversion of sucrose by sucrase, due to an increase in the concentration of the sucrose, is really a linear function of the fluidity of the solution. It is now shown that the diminution in the velocity of inversion due to the presence of the products of inversion or of dextrose or lævulose separately is simply a physical effect due to an increase in the viscosity of the solution. In all these cases, the velocity of hydrolysis is a linear function of the fluidity of the solutions. W. G.

**The Structure of Atoms.** A. BERTHOUD (*Arch. Sci. phys. nat.*, 1919, [v], 1, 473—496).—A résumé of recent work on this subject. W. G.

**Modification of Bohr's Atomic Model.** F. KIRCHOF (*Zeitsch. physikal. Chem.*, 1919, 93, 623—633).—A theoretical paper in which the author puts forward an hypothesis of the constitution of the atom which, although based on Bohr's hypothesis, differs in many details. The outside ring is assumed to contain 8 electrons and atoms, and never more; thus, carbon and silicon contain 4 electrons and can combine with 4 atoms, fluorine and chlorine contain 7 electrons and may combine with 1 atom, argon contains 8 electrons in its outside ring, and so is saturated and cannot combine at all. This view is in keeping with Abegg's contravalency hypothesis, and it follows that the number of electrons in the outside ring is the same as the contravalency of the element. The author suggests that the second ring, from the nucleus, containing 8 electrons and beginning with sodium, is responsible for the *K*-series spectrum, whilst the *L*-series spectrum is due to a ring with 12 electrons (third from nucleus) and commences with zinc; the *M*-series spectrum is due to a ring (fourth from the nucleus) containing 14 electrons and commencing with gold. J. F. S.

**Spectroscopic Proof of Electrical Fields on the Surface of Chemical Atoms.** J. STARK (*Ann. Physik*, 1919, [iv], 60, 196—200).—A theoretical paper in which, from a consideration of the third subsidiary series of lithium and helium, and of the conditions under which these series become visible, it is shown that electric fields are situated on the surface of the atoms. J. F. S.

**Nature of the Forces between Atoms in Solids.** RALPH W. G. WYCKOFF (*J. Washington Acad. Sci.*, 1919, 9, 565—592).—A theoretical paper in which the structure of the atom is discussed with reference to the nature of the forces operating between atoms; it is emphasised that only the arrangement of the outside electrons has a bearing on the phenomena usually described as chemical. The arrangement of the inner electrons cannot be deduced from chemical data alone. The outstanding fact is the tendency to form "closed clusters" of 8 or 16 electrons. A number of typical compounds are considered with reference to the nature of the forces producing them. All compounds lie between the two extremes of "polar" and "non-polar" compounds. A simple method of representing the type of combination in a given compound is put forward. Solid substances are classified, according to the nature of the forces of combination, into molecule-forming, polar, and valency compounds. The phenomena of adsorption, solubility, ionisation in solution, formation of complex ions, and molecular complexes are discussed from this point of view. J. F. S.

**Derivation of Chemical Relationships from the Electron Theory.** HEINRICH TEUDT (*Zeitsch. anorg. Chem.*, 1919, 108, 137—160).—In a previous paper (A., 1919, ii, 330) was outlined a theory of the periodic system of the elements based on certain assumptions regarding the mode of arrangement of the electrons in the atoms. This theory is now extended to a consideration of the combination of atoms to form molecules and compounds. Since the inner electrons rotate in a series of rings as near to the equator of the atom as possible, it follows that the positive lines of force due to the positive charge of the nucleus are concentrated at the poles of the atom and attract valence electrons to this region. Combination between atoms therefore takes place at the poles of the atoms, and the electrons held in common between the combining atoms rotate in an orbit between the poles of the combined atoms. In addition to the attractive force between the valence electrons and the positive nucleus of opposing atoms, forces of attraction between the electrons of the inner rings and the positive spaces between them also come into play, and it is shown that, in the case of two atoms of a metalloid element, the net result is an attraction, whilst with two atoms of a metal a repulsion results, or a much weaker attraction. This explains why metalloids generally form polyatomic molecules, whilst the molecules of the metals are monatomic. Similar considerations explain the stability of compounds of different metalloid elements and the ionisation of salts

of the lithium fluoride type. The cause of odour in chemical compounds is traced to the oscillations of the valence electrons in their orbits between the poles of combined atoms. E. H. R.

**Mathematical Proof that the Atomic Weights are Integers when  $O = 16$ .** HAWKSWORTH COLLINS (*Chem. News*, 1919, 119, 247—248).—When the elements are written down in ascending order of atomic weight, it is found that, of the first 25, 21 have values assigned to them which differ by less than 0.5% from integers. The probability that this has happened by accident is 1 in a billion. The five exceptions to this are:  $Gl = 9.1$ ,  $Mg = 24.32$ ,  $Ne = 20.2$ ,  $Si = 28.3$ , and  $Cl = 35.46$ . Of these, neon need not be considered, because it is probably a mixture. If the atomic weights of the remaining elements are reduced by the same proportion, they become  $Gl = 9.00$ ,  $Mg = 24.00$ ,  $Si = 28.00$ , and  $Cl = 35.00$ . The atomic weights are dependent on that of chlorine, so that an error in chlorine would affect the others in the same way. The probability that this is due to an accident is 1:100,000. The author therefore draws the conclusion that all atomic weights are integers when the standard  $O = 16$  is adopted. J. F. S.

**Is the Ratio of the Atomic Weights  $O = 16 : Ag = 107.88$  Correct?** ALOIS BILECKI (*Zeitsch. Anorg. Chem.*, 1919, 108, 113—118).—It has been shown (A., 1917, ii, 197) that the atomic weights of silver, 107.88, bromine, 79.991, and chlorine, 35.46, are multiples of the number  $n_1 = 0.307350427$ . Thus,  $Ag = 351n_1$ ,  $Br = 260n_1$ , and  $Cl = 115\frac{3}{4}n_1$ . On the other hand, the atomic weights of oxygen and other elements determined with reference to oxygen are multiples of the number  $n = 0.3076923$  that of oxygen being  $16 = 52n$ . An examination of the published determinations of the atomic weight of manganese shows that, when this is determined from ratios involving the halogens and silver, for example,  $2Ag : MnBr_2$  or  $2AgCl : MnCl_2$ , the number 54.932 is obtained, which is practically equal to  $178\frac{3}{4}n_1 = 54.9388$ . When, however, the atomic weight is determined from the analysis of the sulphate, that is, from such ratios as  $MnSO_4 : MnO$ ,  $MnO : 4O$ , the number 55.0 is obtained, which is equal to  $178\frac{3}{4}n$ . In the case of zinc, also, similar differences are shown between the atomic weights determined with respect to halogens on the one hand and oxygen on the other. It is suggested, on account of these considerations, that, if the atomic weight of silver is taken as 107.88, that of oxygen should not be 16, that is,  $52n$ , but  $52n_1$ , that is, 15.982. In the same way, the atomic weight of sulphur should be 32.026 instead of 32.06. E. H. R.

**The Derivation of Valency Laws. The Principle of Cationic and Partial Valencies.** HUGO KAUFFMANN (*Ber.*, 1919, 52, [B], 1422—1435).—See this vol., i, 50.

**Periodic Precipitates.** The late LORD RAYLEIGH (*Phil. Mag.*, 1919, [vi], 38, 738—740).—Periodic precipitates are best demon-

strated as follows. A glass lantern-slide is carefully cleaned and placed absolutely level. To 5 c.c. of a 10% solution of gelatin, one drop of a concentrated solution of sodium arsenate is added, and poured over the plate while hot. When it is quite set, but before it can dry, a drop of silver nitrate solution containing a trace of nitric acid is allowed to fall on the plate. A series of rings of periodic precipitates of silver arsenate is obtained by this procedure. The greater the concentration of the diffusing solution, the closer the rings are together. The periodicity is supposed to originate from the difficulty of precipitation without a nucleus. One ring having been formed, precipitation occurs thereat until the silver nitrate solution has diffused to a place where a sufficiency of sodium arsenate solution remains to render possible new precipitation. The interval between successive rings increases with increase of distance from the centre of diffusion. Periodic structure is also exhibited when a few drops of a cold saturated solution of copper sulphate and salicin to which is added 3% of strong syrup (sugar) are spread on a microscope slide and warmed, excess of liquid being removed, and the plate kept at about 17° above the ordinary temperature until crystallisation sets in, and then cooled. A polarising microscope reveals a structure periodic some thousand times per centimetre.

J. S. G. T.

**History of the Discovery of the so-called Liebig's Condenser.** R. A. (*Parfumerie Moderne*, 1919, **12**, 10—12; from *Chem. Zentr.*, 1919, iii, 209).—The discovery of the counter-current principle in condensers is not attributable to Liebig, but was made independently by a Frenchman, whose name is unknown, in the year 1770, by Christian Weigel in 1771, and by a Finn, Jean Gadolin.

H. W.

**Filter Funnel.** ERICH LEHMANN (*Chem. Zeit.*, 1919, **43**, 726).—The stem of the funnel is divided so as to form two narrow channels; the part connecting the upper portion of these two channels forms a support for the point of the filter paper contained in the funnel.

W. P. S.

**Method for Rapid Filtration.** J. DOCTERS VAN LEEUWEN (*Chem. Weekblad*, 1919, **16**, 1424—1425).—The author has obtained satisfactory results with the method proposed by Noyes (*Int. Sugar J.*, May, 1919; from *Chem. Anal.*), in which, by tearing off a corner from one or two thicknesses of the folded filter paper, an unbroken stream of liquid is obtained in the stem of the funnel, filtration being thereby accelerated.

W. J. W.

**Tait Vortex-rings and Colloidal Sulphur: with Lecture Experiments.** I. GUARESCHI (*Atti R. Accad. Sci. Torino*, 1917—1918, **53**, 321—334).—Vortex-rings of mixed air and ammonium chloride vapour are so stable that they are able to traverse successively several layers of water or other liquid, the conclusion drawn by the author being that the ammonium chloride is present



in the colloidal condition. Good rings are also obtainable by forcing sulphur trioxide or phosphoric oxide vapour, by squeezing a rubber bulb, through a U-tube containing water, etc.; the orifice through which the rings issue may be either circular or square. Various procedures are described for obtaining rings by passing the above vapours, mixed with other vapours and gases, through different substances.

When hydrogen sulphide and air are passed together through a U-tube containing either fresh soda-lime or a mixture of quicklime and yellow mercuric oxide, vivid incandescence is observed at a certain point in the U-tube. In the latter case, when the resultant mixture of hydrogen sulphide and sulphur dioxide is passed through water, the latter becomes milky owing to the deposition of colloidal sulphur, which is precipitated in arborescent formation and falls from the surface to the bottom of the liquid in spirals, each of which is terminated by a ring similar to the vortex-rings. A modification of this experiment, for use as a lecture demonstration, is described.

T. H. P.

### **Soluble Aluminium Phosphate. A Lecture Experiment.**

OLOF SVANBERG (*Zeitsch. anorg. Chem.*, 1919, **108**, 70—72).—When to a 1% solution of aluminium chloride, neutralised with ammonia if it has a slight acid reaction, are added a few drops of a 1—2% solution of potassium dihydrogen phosphate, both being coloured yellow by the addition of a drop of methyl-orange solution, the colour of the mixture immediately becomes red without the formation of any precipitate or of any turbidity. When the solution is warmed a precipitate comes down, but there is no further colour change. Measurements were made of the hydrogen-ion concentration in binary solutions of the two salts, and it was found that a maximum occurs with about 40 mols. % of potassium dihydrogen phosphate. Salts of calcium, magnesium, zinc, or cadmium do not give the colour change with the phosphate. Glucinum sulphate does give the reaction, but it is much more sensitive to excess of phosphate.

E. H. R.

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### Inorganic Chemistry.

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**Preparation and Testing of Hydrogen of a High Degree of Purity.** JUNIUS DAVID EDWARDS (*J. Ind. Eng. Chem.*, 1919, **11**, 961—963).—An apparatus has been devised as a substitute for the Kipp generator. It consists of two connected cylinders, into one of which the zinc is introduced, whilst a tube through a rubber cork in the bottom is connected with the acid flask. The outlet tube has a side connexion, which dips into mercury and serves as a pressure indicator and as a safety valve. Air is exhausted from the cylin-

ders, the acid flask nearly filled with dilute sulphuric acid, and a few fragments of zinc introduced to sweep out the air before the flask is attached to the cylinders. The acid is drawn up into the generator by turning a tap at the top and opening a vent in the stopper of the acid flask. Pure hydrogen is thus at once obtained and fresh acid introduced without admitting air. Tests made in comparison with pure electrolytic hydrogen by means of the interferometer (A., 1915, ii, 478) showed that hydrogen produced by this apparatus contained less than 1 part in 10,000 of impurities. In similar tests of the gas produced by a Kipp generator 83·86% of hydrogen was found to be present seventeen minutes, and 99·97% forty-two minutes after starting. [See also *J. Soc. Chem. Ind.*, 1920, 19A.] C. A. M.

**New Experiment to Demonstrate the Minute Mass of a Hydrogen Atom.** FR. BÜRKI (*Helv. Chim. Acta*, 1919, 2, 703—704).—A yellowish-green fluorescence is distinctly observable in a darkened room when a beam of light is passed through 0·5 c.c. of a solution prepared by dissolving 0·4 mg. of fluorescein in 10 litres of water. The total quantity of hydrogen which can be furnished by the weight of fluorescein present in this solution is  $6 \times 10^{-11}$  grams, which therefore gives an upper limit for the mass of the hydrogen atom. The figure is greatly in excess of the generally accepted value. H. W.

**Composition of the Atmosphere.** AUGUST KROGH (*Math. fysiske Meddelelser*, 1919, 1, No. 12, 1—19).—Our knowledge of the composition of the atmosphere is still quite uncertain, especially in regard to hydrogen and the relation between oxygen and nitrogen. Until very recently little attention has been paid to the variation in the mixture composing the atmosphere at different altitudes. Wegener claims that at a height of 70 km. hydrogen must be the chief constituent of the earth's atmosphere. Benedict has shown by 200 analyses extending over a period of nine months that the percentage of oxygen at the surface or laboratory level never varied more than  $\pm 0\cdot01$  from the average, and that of carbon dioxide never more than  $\pm 0\cdot005$ . The author describes a new gas analysis apparatus with three gas burettes, one for moving the air sample to and from the absorption pipettes, and for saturating the air with moisture, a second convenient in size for measuring the air before and after the absorption of carbon dioxide, and a third which holds the residual gas after the absorption of oxygen. The author discusses general means for reaching more accurate and constant results. The heated platinum wire method has been applied for the detection of combustible gases, and the conclusion is drawn that hydrogen or other combustible gas is present in an amount which is probably less than 0·002%. The percentage of carbon dioxide in the streets of Copenhagen is usually increased by 0·001—0·007. The need of a thorough research to establish the absolute average composition of pure atmospheric air with more certainty, and a study

of its variations, especially in the higher strata of the atmosphere, is strongly urged. Accurate analyses of samples taken simultaneously from aeroplanes at various heights up to 5 or 6 km. would give valuable information in regard to mixing by vertical currents. Automatic sampling by balloons is suggested. Up to the present time the absolute composition of atmospheric air at the earth's surface has been found to be  $\text{CO}_2$ , 0.030%;  $\text{N}_2$ , 79.022%; and  $\text{O}_2$ , 20.948%.

CHEMICAL ABSTRACTS.

**Nitrogen Generator for Laboratory Use.** W. L. BADGER (*J. Ind. Eng. Chem.*, 1919, **11**, 1052—1053).—A wide-necked 2-litre bottle is closed with a rubber stopper through which passes one end of a Liebig condenser jacket (without the condenser tube); the lower water-inlet is sealed off, and the upper one is connected with a side-tube which extends through the stopper to the bottom of the bottle. A bulb with delivery tube is sealed on the upper end of the jacket. The bottle is packed with copper wire, and as much ammonia (1:1) saturated with ammonium chloride is poured in as the bottle will hold. The jacket is filled with copper turnings. Air is blown in through a tube reaching nearly to the bottom of the bottle; the oxygen is absorbed rapidly, and practically pure nitrogen escapes from the delivery tube. The passage of the air (or nitrogen) causes the solution to circulate slowly up the jacket and through the side-tube into the bottle again. W. P. S.

**The Synthesis of Ammonia at Very High Pressures.** GEORGES CLAUDE (*Compt. rend.*, 1919, **169**, 1039—1041).—Having previously shown the possibility of using very high pressures for industrial purposes (*ibid.*, 649), the author has studied the synthesis of ammonia at these high pressures, and finds that at a pressure of 1000 kilos./cm.<sup>2</sup> and at a temperature of 536° the yield of ammonia is over 40%. The zone of temperature within which this reaction takes place at a reasonable velocity under such a high pressure is 500—700°. W. G.

**Behaviour of the Hydronitrogens [Nitrogen Hydrides] and their Derivatives in Liquid Ammonia. VI. Electrolytic Nitridation of Various Anodes in a Solution of Ammonium Trinitride.** A. W. BROWNE, M. E. HOLMES and J. S. KING (*J. Amer. Chem. Soc.*, 1919, **41**, 1769—1776. Compare A., 1911, ii, 1084, 1085; 1913, ii, 583).—Solutions of 1 gram of ammonium azide in 36 c.c. of liquid ammonia were electrolysed at -67°, using anodes of copper, silver, cadmium, aluminium, lead, antimony, iron, and nickel. The gas evolved at both anode and cathode was measured, and the loss of weight of the anode determined. It is shown that copper anodes undergo electrolytic corrosion to an extent indicating the formation of some cuprous azide,  $\text{CuN}_3$ , with cupric azide,  $\text{CuN}_6$ , as the main product. No gas was liberated at the anode. With silver, cadmium, lead, and antimony anodes the corrosion resulted in the formation of normal azides,

$\text{AgN}_3$ ,  $\text{CdN}_6$ ,  $\text{PbN}_6$ , and  $\text{SbN}_9$ , without liberation of gas at the anode. Aluminium, iron, and nickel anodes undergo corrosion, accompanied by the liberation of nitrogen. The aluminium anode became coated with a bulky pyrophoric scale of varying colour and texture. Deep red ferric azide,  $\text{FeN}_9$ , was obtained in solution when an iron anode was employed, but this product was ammonolysed and yielded an ammono-basic ferric azide. A pink deposit was formed on the nickel anode, presumably an ammono-basic nickel azide.

J. F. S.

**Some Properties of Nitrogen Trioxide, Pure or in Solution in Nitrogen Peroxide.** GEORGES BAUME and MARIUS ROBERT (*Compt. rend.*, 1919, **169**, 968—970).—The authors have studied the melting-point and vapour-pressure diagrams of the system nitrogen trioxide–nitrogen peroxide. The melting-point diagram is normal, and has a single eutectic in the neighbourhood of the freezing point of pure nitrogen trioxide. From the vapour-pressure curves between  $-80^\circ$  and  $35^\circ$ , the author deduces the b. p. of pure nitrogen trioxide to be  $-27^\circ/760$  mm.

Pure nitrogen trioxide can only exist at very low temperatures in the solid state or in the liquid state under pressure of nitric oxide. At temperatures above  $-100^\circ$  it dissociates. It is not possible to distil it in a vacuum because of the immediate formation of an atmosphere of nitric oxide at temperatures at which distillation is possible.

W. G.

**Silicon Hydrides. VII. Protosiloxane,  $\text{O}:\text{SiH}_2$ .** ALFRED STOCK and KARL SOMIESKI (*Ber.*, 1919, **52**, [B], 1851—1860. Compare A., 1918, ii, 111).—In the earlier paper it was shown that dibromomonosilane reacts with water to form polymerides of protosiloxane,  $\text{O}:\text{SiH}_2$ . The unimolecular form has now been obtained as a gas by the action of the required amount of water vapour on dichloromonosilane in a very large flask under greatly reduced pressure. It has an extraordinary tendency to polymerise, much more so than the analogous carbon compound, formaldehyde, in consequence of which the flask must be perfectly clean and smooth. Liquid and solid polymerides are formed immediately on condensation. The liquid ones are like benzene, and can be obtained conveniently as a solution by shaking a benzene solution of dichloromonosilane with water. These benzene solutions are fairly stable towards water, but reduce silver nitrate in the cold. They correspond roughly with  $(\text{SiH}_2\text{O})_6$ . The solid polymerides are insoluble. All the polymerides react with sodium hydroxide according to the equation  $\text{SiH}_2\text{O} + 2\text{NaOH} = \text{Na}_2\text{SiO}_3 + 2\text{H}_2$ .

J. C. W.

**Constitutional Formulæ of Kaolinite and other Silicates.** RUDOLF WEGSCHEIDER (*Zeitsch. Elektrochem.*, 1919, **25**, 352).—It is shown that the constitutional formulæ of polysilicates must be written with the silicon atoms joined through oxygen and not directly with one another. Compounds with the silicon atoms directly united are reducing agents and unstable. Further, if the polysili-

ates are considered as having the silicon atoms directly united it will follow that the oxygen atoms must also be directly united, which again will point to instability. The combination of a strongly reducing group,  $-\text{Si}-\text{Si}-$ , with a strongly oxidising group,  $-\text{O}-\text{O}-$ , will, of necessity, give a compound of an extremely unstable character, which is certainly not the case with the polysilicates. [See also Simmonds, T., 1904, **85**, 681; Pukall, A., 1910, ii, 780; Manchot, A., 1910, ii, 1060.] J. F. S.

**Theory of Binary Mixtures. V. Vapour Pressure and Molecular Constitution of Liquid Argon and Argon-Nitrogen Mixtures.** F. DOLEZALEK (*Zeitsch. physikal. Chem.*, 1919, **93**, 585—595. Compare A., 1916, ii, 132).—A theoretical paper, in which, using the experimental data previously published, the association constants are calculated from the saturation pressure of the mixture, and also the molecular constitution of the mixtures and pure argon, the saturation pressures of the liquid mixtures and the constitution of the vapour. It is shown that liquid argon is partly composed of diatomic molecules and has an association constant at  $85.11^\circ$  abs. of  $K=0.20$ . Hence at low temperatures argon possesses chemical affinity, and consequently argon compounds are to be expected at low temperatures. There is therefore no fundamental difference between the inactive gases and other gases, but only a difference of degree. When liquid argon is diluted with liquid nitrogen the diatomic molecules dissociate according to the law of mass action. The vapour tension of liquid argon-nitrogen mixtures, as well as the constitution of the vapour, may be calculated at all concentrations by means of the author's theory of solution (A., 1909, ii, 22). J. F. S.

**Preparation of Metallic Potassium.** FRITZ C. WICKEL and WALTER LOEBEL (D.R.-P. 307175; from *Chem. Zentr.*, 1919, iv, 361).—Accurately measured quantities of metallic sodium and potassium hydroxide are melted together with exclusion of air, so that sodium oxide is formed and potassium is volatilised from the mixture (at about  $670^\circ$ ), and suitably condensed. Hydrogen is obtained as by-product. The process is suitable for the manufacturing scale. H. W.

**The Autoxidation of Sodamide.** HANS SCHRADER (*Zeitsch. anorg. Chem.*, 1919, **108**, 44—48).—The amides of the alkali metals are known to undergo autoxidation, with the formation of nitrite, hydroxide, and ammonia. When finely divided sodamide is exposed to air in presence of a little water, a yellowish-red oxidation product is formed, which is now shown to be a peroxide, probably of the formula  $\text{NaNH}_2\text{O}_2$ . The peroxide formed was estimated by adding the product to a cold saturated solution of barium chloride, when barium peroxide was precipitated, and was estimated in the usual way. It was found that a sample of sodamide gave in fifty-eight days at ordinary temperature 0.44

mol. % peroxide and 6.9% nitrite. In dry air, autoxidation does not take place at the ordinary temperature, but at 100° to 110° the peroxide is slowly formed. The peroxide is stable in dry air, but in moist air is changed into a white substance, the aqueous solution of which gives the peroxide reaction. E. H. R.

**Solubility and Fusion Relations at High Temperatures and Pressures.** GEORGE W. MOREY (*J. Eng. Club, Philadelphia*, 1919, **35**, 509—519).—An address. The preparation of the compounds *monopotassium aluminate*,  $K_2O \cdot Al_2O_3$ , large, octahedral crystals, and *monopotassium ferrite*,  $K_2O \cdot Fe_2O_3$ , large, red, octahedral crystals, decomposed by water below 500°, is mentioned.

CHEMICAL ABSTRACTS.

**The Properties of Ammonium Nitrate. I. The Freezing Point and Transition-temperatures.** REGINALD GEORGE EARLY and THOMAS MARTIN LOWRY (*T.*, 1919, **115**, 1387—1404).

**Action of Bromine on Calcium Carbide.** EDWARD BARNES (*Chem. News*, 1919, **119**, 260—261).—Liquid bromine acts slowly on calcium carbide at ordinary temperatures, producing carbon hexabromide and calcium bromide. 4.5 Grams of finely powdered calcium carbide, treated with 45 grams of purified dry bromine in a 50 c.c. bottle for five months, gave a product which, after removal of excess of bromine, weighed 32.4 grams and contained 22 grams of hexabromoethane, 8.8 grams of calcium bromide, and 0.2 gram of unchanged calcium carbide. Calcium carbide and bromine heated in sealed tubes at 100°, until no further action was apparent, produced carbon and calcium bromide. Dry chlorine was found to have no action on calcium carbide exposed to it at the ordinary temperature for two months. S. S. A.

**Reduction of Barium Nitrate by the Alternating Current.** P. WENGER and A. LUBOMIRSKI (*Ann. Chim. anal.*, 1919, [ii], **1**, 339—342).—With lead electrodes, the yield of nitrite increases with the amperage, but with mercury electrodes the maximum yield is obtained with 0.6 ampere; the yield also increases with temperature in the case of lead electrodes, and decreases with aluminium or zinc electrodes. Temperature has little, if any, effect when copper, cadmium, or magnesium electrodes are employed. The oxygen liberated from the nitrate combines with the electrode, forming suboxides (copper, mercury, cadmium, and tin electrodes), hydroxides (lead, zinc, aluminium, and magnesium electrodes), or oxides (nickel and silver electrodes). The nitrate is not reduced by the metallic electrodes unless the current is passing. W. P. S.

**Purification of Magnesia. Conditions in which Periclase or Crystalline Magnesia is Formed.** J. MEUNIER (*Bull. Soc. chim.*, 1919, [iv], **25**, 560—562).—Magnesium oxide may be freed from contained calcium by igniting the material at a red heat and

subsequently, after cooling, extracting it with successive quantities of a 10% sucrose solution until the last extract does not give any turbidity with ammonium oxalate. If such material is then washed with water, dissolved in hydrochloric acid, the solution evaporated to dryness, and the residue gradually heated in a covered crucible until it attains a red heat, magnesium oxide is obtained in the form of crystals of periclase on the lid and sides of the crucible and on the surface of the amorphous oxide in the crucible. The material so obtained is very pure. W. G.

**Concentrated Thallium Amalgams: their Electrochemical and Thermochemical Behaviour; Densities and Freezing Points.** THEODORE W. RICHARDS and FARRINGTON DANIELS (*J. Amer. Chem. Soc.*, 1919, **41**, 1732—1768).—The electromotive force, density, specific volume, specific heat, heat of dilution, and freezing point of thallium amalgams up to a concentration of 40.9% thallium have been experimentally determined. The heat of solution of thallium in mercury and in various amalgams has also been determined. The *E.M.F.* measurements were made at 20°, 30°, and 40°, and are shown to be much greater than demanded by the simple concentration law. The temperature-coefficients of the *E.M.F.*'s have been calculated for the various amalgams, and they are found to be less than is demanded by the gas law and vary as the concentration increases. The solution volume of thallium is remarkably constant, varying only from 17.47 to 17.51, but it is somewhat larger than the specific volume (17.21) of thallium. Thallium, therefore, must expand on amalgamation. The coefficients of expansion were calculated from these results, and found to diminish with increasing concentration. The heat capacities were found to be distinctly larger than the sum of the heat capacities of the thallium and mercury in the amalgam. This excess is greater in dilute than in concentrated amalgams. The heat of dilution with mercury was determined at 20°, and from the results the values at 30° and 325° were calculated. Although the heat of dilution of thallium amalgam is a very different effect from the transfer of thallium from one amalgam to another, it is shown that either of these effects may be calculated from the other. Within the limits of experimental error, the heat effects in the cells of which the *E.M.F.* was measured may be calculated from either the heat of dilution of the amalgams, or the heat of solution of thallium in the amalgams, or the temperature-coefficient of the *E.M.F.*, each of these three methods giving essentially identical results within the limits of experimental error. The freezing points of amalgams containing from 16 to 45 atomic % of thallium were found to give a curve indicating conclusively the existence of the solid compound  $Tl_2Hg_5$ . The single potential of pure electrolytic thallium was found to be about 2.5 m.v. more negative than that of saturated thallium at the ordinary temperature. J. F. S.

**Nitrous-Nitric Complexes of Thallium.** L. ROLLA and G. BELLADEN (*Gazzetta*, 1919, **49**, ii, 217—224).—Thallium nitrite,



like barium, strontium, and calcium nitrites (compare Vogel, A., 1903, ii, 591), has a specific electrolytic conductivity below that of the corresponding nitrate, and undergoes normal dissociation. The *E.M.F.* of the cell, thallium amalgam | *N*/10-thallium nitrite | normal electrode, is 0.667 volt at 25°, the same value being obtained if the nitrite is replaced by the nitrate.

Peters found that lead nitrate and nitrite interact in solution, forming well-defined compounds containing both salts. Similarly, thallium nitrite and lead nitrate react, yielding compounds containing Pb, Tl, NO<sub>3</sub>, NO<sub>2</sub>, and OH. With potassium nitrite and thallium nitrate, however, despite wide variations in the concentrations of the reacting solutions, no product containing potassium could be obtained; the nitrate-nitrites formed, although they have compositions differing greatly from those of Peters' salts, are stable and may be recrystallised unchanged. If the two reacting salts are taken in molecular proportions, the resultant product has the percentage composition Tl 76.65, NO<sub>3</sub> 20.58, and NO<sub>2</sub> 2.76, whilst in the proportion TlNO<sub>3</sub> and 2KNO<sub>2</sub> the compound obtained has the formula Tl<sub>3</sub>N<sub>3</sub>O<sub>8</sub>, the ratio of NO<sub>3</sub> to NO<sub>2</sub> in the complex ion being 2:1. With 3 mols. of potassium nitrite and 1 mol. of thallium nitrate, the product has the percentage composition Tl 82.78, NO<sub>3</sub> 6.64, NO<sub>2</sub> 5.80, and OH 4.78, and with 4 mols. of the nitrite to 1 mol. of the nitrate the composition is Tl 86.22, NO<sub>3</sub> 1.27, NO<sub>2</sub> 4.17, and OH 8.34. T. H. P.

**Investigations on some Rapid Low Temperature Reactions by means of Heating Curves.** J. ARVID HEDVALL and NILS VON ZWEIFBERGK (*Zeitsch. anorg. Chem.*, 1919, **108**, 119—136).—In a previous paper (A., 1919, ii, 26) it was shown that the decomposition of barium peroxide takes place at a much lower temperature in presence of all modifications of silica than when heated alone, a certain amount of barium silicate being formed at the same time. The behaviour of a great number of other oxides when heated with barium peroxide has now been studied by examining the heating curves of the mixtures in molecular proportions. Cuprous oxide reacts violently with barium peroxide at about 130° and is completely oxidised to cupric oxide. The latter decomposes barium peroxide catalytically, the optimum temperature being about 660°. Magnesium and calcium oxides start the decomposition of the peroxide at 250° and 310° respectively, whilst zinc oxide brings about slow decomposition between 200° and 370°, and at the same time forms barium zincate. Purely catalytic action is shown by cadmium oxide, lanthanum oxide, and cerium peroxide, whilst zirconium oxide and stannous and stannic oxide are without action. Alumina acts catalytically and forms an aluminate. Titanium oxide and barium peroxide in molecular proportions, when heated below 300°, evolve oxygen slowly; above 300° a titanate is formed, probably BaTiO<sub>3</sub>. When the proportions 2BaO<sub>2</sub> to TiO<sub>2</sub> are used, a basic titanate, completely soluble in acetic acid, is formed. Litharge and barium peroxide between 300° and 400°

give no oxygen, but form a brown product, the nature of which has not been determined. Above  $500^{\circ}$ , much oxygen is evolved and a product formed, probably  $\text{Ba}_2\text{PbO}_4$ , which leaves a residue of lead peroxide when treated with nitric acid. Vanadium pentoxide reacts vigorously with barium peroxide. When equimolecular proportions are used, reaction begins at  $215^{\circ}$  and is ended at  $530^{\circ}$ , barium metavanadate,  $\text{Ba}(\text{VO}_3)_2$ , being formed. With  $2\text{BaO}_2$ , the metavanadate is first formed, but at  $375^{\circ}$  a second, very vigorous, reaction starts, and the colour changes from brown to white, the product formed being apparently  $\text{Ba}_2\text{V}_2\text{O}_7$ . Tantalum pentoxide also reacts vigorously, with formation of a tantalate. When arsenic trioxide is heated with barium peroxide (3 mols.), arsenic pentoxide is first formed at  $310^{\circ}$  to  $410^{\circ}$ , and above  $465^{\circ}$  evolution of oxygen begins and barium arsenate is formed. Antimony trioxide behaves differently, as at  $200^{\circ}$  oxygen is evolved with almost explosive violence. Bismuth trioxide starts a gradual evolution of oxygen at about  $250^{\circ}$ , and higher oxides of bismuth, or compounds of these with barium oxide, appear to be formed. Chromium sesquioxide is rapidly oxidised above about  $225^{\circ}$  without evolution of oxygen, barium chromate being formed. The oxides  $\text{MoO}_3$ ,  $\text{WO}_3$ ,  $\text{U}_3\text{O}_8$ , and  $\text{UO}_3$  all cause evolution of oxygen and form molybdates, tungstates, and uranates respectively. The lower oxides of manganese are all oxidised, barium manganate being formed. Ferric oxide acts catalytically, and at the same time ferrate is formed. Nickel and cobalt oxides both act catalytically, and are at the same time changed into higher oxides, which, however, do not agree in their properties with the known peroxides of these metals.

E. H. R.

**Basic Exchange in Permutite.** V. ROTHMUND and G. KORNFIELD (*Zeitsch. anorg. Chem.*, 1919, **108**, 215—225).—In a previous paper (A., 1918, ii, 315), basic exchange between univalent metals in permutite was studied. The inquiry has now been extended to bivalent metals, with the study of the exchange between copper permutite and the nitrates of magnesium, calcium, strontium, and barium, and it has been confirmed that, with equivalent ions, the reaction is independent of the dilution. The tendency to permutite formation is least with magnesium, and increases steadily from calcium to barium. For the equilibrium between uni- and bi-valent ions, the equation takes the form  $(c_1')^2/c_2' \cdot (c_2/c_1^2)^{\beta} = K$ , and this formula has been verified for the exchange between silver permutite and barium nitrate, and for that between calcium and sodium in sodium and calcium permutites. In the latter case a gap was found in the series, showing that calcium and sodium permutites are not completely miscible. The equilibrium for these cases is not independent of the dilution. A few experiments on the exchange between lanthanum and silver permutites showed that in this case the dilution has a marked influence on the equilibrium.

E. H. R.

**Preparation of Colloidal Mercury by Cathodic Disintegration.** A. GUTBIER and G. L. WEISE (*Kolloid Zeitsch.*, 1919, **25**, 97—100).—Colloidal solutions of mercury may be prepared by

striking an arc between a clean mercury surface and a thin platinum foil cathode under water. The most suitable current to employ for the purpose is 3—4 amperes at either 110 or 220 volts. By this means, at ordinary temperatures, the sols are obtained, which have a grey colour, and change from light grey to bluish-grey and then to grey as the concentration increases. The sols are not very stable; on keeping, they coagulate in about twenty-four hours, and are coagulated by very small quantities of electrolytes. In all cases, the coagulation is irreversible. Much more stable sols are produced when a protecting colloid is present; thus, using 1:10 or 1:50 gum arabic solution in water, grey sols are produced, which may be preserved for ten to fourteen days. These sols are also very sensitive to electrolytes and are irreversibly coagulated by the addition of alcohol.

J. F. S.

**Scandium.** R. J. MEYER and B. SCHWEIG (*Zeitsch. anorg. Chem.*, 1919, **108**, 303—317).—It was shown in a previous paper (A., 1914, ii, 369) that the atomic weight of scandium given in the International tables cannot be accepted as a final figure. The impurities likely to be present in scandium preparations separated by the usual methods from the other rare earths are traces of thorium and of the elements of the yttrium earths. It has now been found that complete separation of scandium from these impurities can be effected by fractional crystallisation of scandium formate or of ammonium scandium fluoride,  $(\text{NH}_4)_3\text{ScF}_6$ . A sample of scandium oxide, the spectrum of which showed no trace of yttrium lines and only faint traces of those of thorium and ytterbium, was fractionated by the formate method, and when the most soluble fraction was examined spectroscopically, the lines of all these elements showed up very strongly, showing that the spectroscopic test for them is not so sensitive as is usually supposed. The least soluble fraction appeared to be pure scandium formate, and the atomic weight of the metal, determined by the sulphate method, was 45.33 to 45.35. Ammonium scandium fluoride was crystallised from hot, weakly ammoniacal aqueous solution. The impurities separated first from the hot solution, and after these had been filtered off, the solution was allowed to cool. After two or three such crystallisations, the spectrum of the double salt showed no signs of the presence of foreign elements. Atomic weight determinations on the pure materials thus prepared were made by Hönigschmidt by analysis of scandium bromide, the mean result of a series of experiments pointing to 45.1 as the true atomic weight of scandium (A., 1919, ii, 285—286). This is one whole unit above the accepted value. The present authors confirm Hönigschmidt's conclusion that an exact determination of the atomic weight cannot be made by the sulphate method, on account of the impossibility of preparing a pure scandium sulphate free from both basic and acid salts.

E. H. R.

**The Changes Undergone by certain Alloys of Aluminium.**

LÉON GUILLET (*Compt. rend.*, 1919, **169**, 1042—1043).—It has

been shown previously (A., 1902, ii, 264) that certain alloys of aluminium with either iron, manganese, or nickel rapidly crumble to powder in the air. These experiments have been repeated, and this time the alloys of aluminium with iron or nickel remained stable. The aluminium-manganese alloy, containing 85.4% of manganese, crumbled very rapidly in the air, but more slowly in oxygen, nitrogen, or hydrogen, without gaining in weight. The change is to an allotropic modification. Similarly, an alloy of aluminium and antimony fell to powder in moist air, but not in dry air, but in this case the change was chemical, oxidation taking place.

W. G.

**The Ternary System, Aluminium-Copper-Zinc, with Reference to Zinc in Particular.** V. JAREŠ (*Int. Zeitsch. Metall.*, 10, 1—44; from *Chem. Zentr.*, 1919, iii, 512—514).

—The literature of the binary systems Al-Zn, Al-Cu, and Cu-Zn is critically reviewed, in addition to that of the ternary system, with reference to copper. The author has chiefly investigated the portion of the system Al-Zn-CuAl-CuZn<sub>4</sub>. This can be resolved into four equilibria triangles, to each of which a ternary, non-variant, pseudo-eutectic point belongs, which (except in one doubtful case) lies outside the equilibrium triangle. At 424°, with 68% zinc, 12% copper, and 20% aluminium, reaction is expressed by the scheme: aluminium mixed crystals + fused mass  $\rightleftharpoons$  Al<sub>2</sub>Zn<sub>3</sub> + CuAl<sub>2</sub>; at 418°, with 72% zinc, 11.5% copper, 16.5% aluminium, the equation is CuAl<sub>2</sub> + fused mass  $\rightleftharpoons$  Al<sub>2</sub>Zn<sub>3</sub> + CuAl; at 406°, with 79.5% zinc, 9% copper, and 11.5% aluminium, equilibrium occurs as follows: Al<sub>2</sub>Zn<sub>3</sub> + CuZn<sub>4</sub>  $\rightleftharpoons$  fused mass; at 385°, with 94% zinc, 1% copper, 5% aluminium, the reaction is CuZn<sub>4</sub> + fused mass  $\rightleftharpoons$  Al<sub>2</sub>Zn<sub>3</sub> + Zn, mixed crystals; at 590°, with 76% zinc, 23% copper, 11% aluminium, equilibrium occurs thus:  $\delta$  + fused mass  $\rightleftharpoons$  CuAl + CuZn<sub>4</sub>. Ternary compounds were not observed. The alloys were prepared by melting the requisite amounts of the pure metals in unglazed crucibles in an electric furnace with alloys containing 20, 50, and 70% of copper. The temperatures were measured with platinum-platinum rhodium or with silver-nickel thermo-elements (calibrated by the m. p.'s bismuth 269°, lead 327°, zinc 419°, Sb 630.5°). The changes in the solid alloy resulting from the decomposition of the compound Al<sub>2</sub>Zn<sub>3</sub> at 256° were not investigated. The microscopic observations were made with sections etched with aqueous sodium hydroxide solution (2%) or alcoholic picric acid (2%).

The mechanical properties of alloys of aluminium, copper, and zinc, rich in the latter, have been investigated; to secure a near approach to the technical alloys, commercial zinc containing about 1% of lead was used. The hardness of slowly cooled specimens in the system Zn-Al increases rapidly with the aluminium content to about 70 at 10% Al, remains constant to about 20% Al, and then increases very slowly; it reaches a maximum in the system Zn-Cu at about 5% Cu, sinks to a minimum at 12—14% Cu, and subsequently increases very rapidly. The minimum of the Zn-Cu alloy

is also observed in the ternary system Al-Cu-Zn in slowly cooled specimens, but is absent from quickly cooled specimens; the hardness increases considerably more uniformly. The tenacity of Cu-Zn alloys shows a maximum at about 10% Cu, whilst that of Zn-Al alloys increases fairly rapidly with addition of copper to about 8–10% Cu, and then sinks. Fractured surfaces of zinc become finer by addition of aluminium without altering the usual structure; addition of copper causes little alteration in the region of the zinc mixed crystals, but subsequently the fracture is more finely granular. The compressibility of alloys of zinc 90%, Cu 6%, and Al 4% has also been investigated. The tenacity and hardness of brass or ordinary bronze is readily attained in Al-Cu-Zn alloys, but the brittleness of the latter make them an imperfect substitute for the former.

The technical possibilities of Al-Cu-Zn alloys rich in the latter are discussed. The maximum useful copper content is estimated at about 10%, the minimum at about 4%. Aluminium should not exceed 5%, and should be diminished with increasing amounts of copper. The alloys are not suitable for steam; they oxidise too readily, only withstand moderate pressure, and are corroded by many salt solutions, alkalis, and natural waters. They can only be used with caution in making parts subject to considerable mechanical strain. They are frequently useful for fine mechanical work, such as physical instruments.

H. W.

**The Ternary Systems,  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  and  $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ .** A. MEISSNER (*Zement*, 8, 296–298, 308–310; from *Chem. Zentr.*, 1919, iii, 511).—The temperature-concentration relationships in the first system of the different crystalline phases in equilibrium with the liquid phases have been investigated, and the results are expressed in diagrams and by a model. A ternary compound,  $2\text{MgO}, \text{Al}_2\text{O}_3, \text{SiO}_2$ , unstable at its m. p. and showing considerable tendency to the formation of mixed crystals, has been observed in two forms; the unstable,  $\mu$ -variety crystallises from glasses at a temperature of about  $950^\circ$ , and passes at a somewhat higher temperature into the stable  $\alpha$ -variety. The properties of both forms, more particularly of the  $\alpha$ -form, are similar to those of the mineral cordierite. The system  $\text{CaO-Al}_2\text{O}_3\text{-MgO}$  is comparatively simple, since it does not yield a ternary compound which is stable in the presence of the liquid phase. Its investigation, therefore, is concerned with the equilibrium of the components  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{MgO}$ , and of their binary compounds,  $3\text{CaO}, \text{Al}_2\text{O}_3$ ,  $5\text{CaO}, 3\text{Al}_2\text{O}_3$ ,  $\text{CaO}, \text{Al}_2\text{O}_3$ ,  $3\text{CaO}, 5\text{Al}_2\text{O}_3$ ,  $\text{MgO}, \text{Al}_2\text{O}_3$ , in ternary solution. The results are expressed in a series of temperature-concentration diagrams. A new form of aluminium oxide is designated  $\beta\text{-Al}_2\text{O}_3$ . The relationship of each of the forms in the binary system  $\text{MgO-Al}_2\text{O}_3$  demands the presence of solid solutions, the amount of which has been estimated.

H. W.

**Manganese-Bismuth, Manganese-Zinc, and Manganese-Silver Alloys.** PAUL SIEBE (*Zeitsch. anorg. Chem.*, 1919, 108, 161–183).—The condition diagram for manganese-bismuth alloys

has been determined by the cooling curve method. The two metals are not completely miscible. When more than 23% of manganese is present, two layers are formed, the upper consisting of practically pure manganese, whilst the lower is a 23% solution of manganese in bismuth. Five arrest points were found, corresponding with five crystalline phases. The eutectic horizontal is at  $259^{\circ}$ , and the other four horizontals, corresponding with the arrest points, are at  $442^{\circ}$ ,  $597^{\circ}$ ,  $1043^{\circ}$ , and  $1252^{\circ}$ . The last represents a eutectic containing at most 0.5% bismuth, which lowers the melting point of manganese  $13^{\circ}$ . From alloys containing up to 0.5% of manganese, pure bismuth first separates; with 0.5 to 9% of manganese, the first compound separates; from 9% to 11% a second compound, and from 11% to 20% a third. The nature of the compounds has not been determined. Between 23% and 99.5% of manganese there is a complete gap. The microscopic appearance of the different crystalline phases is described. The hardness of the alloys increases with the manganese content. They are ferromagnetic, and this property has been shown to be peculiar to the first compound, crystallising from alloys containing between 0.5% and 9% of manganese.

Alloys of zinc and manganese could be prepared containing only up to 50% of manganese. Those containing from 0% to 11% of manganese show an arrest point at  $416^{\circ}$ , the eutectic point. The eutectic compound contains a very small, undetermined quantity of manganese, which lowers the melting point of zinc  $3^{\circ}$ . The mixed crystal constituent of the eutectic contains 11% of manganese, and a series of mixed crystals are formed containing up to 50% of manganese. The alloys are brittle and increase in hardness as the manganese content increases.

The behaviour of a series of manganese-silver alloys with a number of chemical reagents has been studied. A sharp distinction was found between those containing 0.22 and 0.24 mol. of manganese and those containing 0.26 and 0.28 mol. respectively. The latter pair were readily attacked by silver sulphate solution, with deposition of silver; by copper acetate and copper sulphate, with deposition of copper; and by sulphuric and hydrochloric acids, with liberation of hydrogen, whilst the former pair, containing less manganese, were unattacked. There was found a similar sharp difference when the electric potentials of the two pairs were compared. Those alloys containing more than 0.25 mol. of manganese appear to behave, both chemically and electrically, practically as pure manganese.

E. H. R.

**Fluoro-salts of Tervalent Manganese.** I. BELLUCCI (*Gazzetta*, 1919, 49, ii, 180—186).—The author has isolated the tervalent manganese fluoro-salt which causes the anomalous results obtained when Lunge's method of estimating nitrous acid by means of permanganate is applied to solutions containing fluorine ions in high concentration (compare A., 1919, ii, 476). This salt,  $K_3MnF_6 \cdot H_2O$ , which belongs to the only known type of fluo-salts of tervalent manganese, may be obtained by the action of nitrous acid in

presence of hydrofluoric acid either on potassium permanganate or on a manganous salt, the nitrous acid acting in the former case as a reducing agent and in the latter as an oxidising agent.

T. H. P.

**The Atomic Weight of Iron.** ALOIS BILECKI (*Zeitsch. anorg. Chem.*, 1919, **108**, 318—320).—In a previous paper, the atomic weights of silver and oxygen were compared through that of manganese (this vol., ii, 26). A similar comparison can be made through the atomic weight of iron. Baxter, by analysis of ferrous bromide, found  $\text{Fe} = 55.8378$  when  $\text{Ag} = 107.88$ , or  $\text{Fe} = 55.90$  when  $\text{Ag} = 108.00$ . By analysis of ferric oxide, Richards and Baxter obtained in two series of experiments 55.90 and 55.883, taking  $\text{O} = 16$ . A careful comparison of the data of the individual experiments establishes the fact that the ratio of silver to oxygen must be 108:16 or 107.88:15.9822, thus confirming the conclusion which was arrived at from a consideration of the atomic weight of manganese.

E. H. R.

**The Penetration of Iron by Hydrogen.** T. S. FULLER (*Trans. Amer. Electrochem. Soc.*, **36**, 16 pp.).—Penetration of iron by molecular hydrogen begins at  $325^\circ$  and increases rapidly with the temperature, but nascent or atomic hydrogen penetrates iron at the ordinary temperature, as shown by these experiments. An iron tube with 1/16-in. walls, connected at the top to a U-tube device for measuring the volume of gas entering the tube through its walls, was immersed in a 1% solution of sulphuric acid. Hydrogen generated on the outside of the tube passed through the walls, the rate varying with the conditions. The rate was greater for a unit immersed without electrical connections than when the unit was used as a cathode, but in the latter case the greater the current the greater is the penetration. The rate also increases with temperature. Copper is not penetrated by nascent hydrogen, but a coating of tin on the iron increases the rate. Results are given for other conditions and electrolytes. It was proved that there was no penetration by acid, but by gas alone.

CHEMICAL ABSTRACTS.

**Tin Hydride. I.** FRITZ PANETH and KARL FÜRTH (*Ber.*, 1919, **52**, [B], 2020—2029).—The authors have applied the method which was successfully used in the study of bismuth hydride (Paneth and Winternitz, A., 1919, ii, 68) to the problem of the isolation of a hydride of tin. An alloy of tin and magnesium, corresponding with the formula  $\text{Mg}_2\text{Sn}$ , is dissolved in 4*N*-hydrochloric or sulphuric acid; the gas which is evolved is filtered through cotton-wool, dried by calcium chloride and phosphoric anhydride, and led through a heated hard-glass tube; a mirror of metallic tin is formed in close proximity to the hot part of the tube, which, when well developed, consists of three zones, a whitish-grey, blackish-grey to black, and finally brown in colour. The reactions of the mirror

are very fully described, the most distinctive of them being the insolubility in cold, concentrated nitric acid, and the formation of purple of Cassius and calomel by gold and mercuric chlorides, respectively, after preliminary treatment of the ring with dry, gaseous hydrogen chloride. Preliminary experiments also show that the gas can be condensed by liquid air and re-evaporated without decomposition, so that its collection in some quantity appears possible. The yields, however, are as poor as in the case of bismuth hydride, only a few thousandths per cent. of the tin of the alloy being converted into the hydride.

[With A. MARSCHALL.]—Preliminary experiment appears to show that lead hydride can exist in the gaseous state. It is formed from the magnesium-lead alloy in yield which is worse than in the cases of bismuth or tin, but better results are obtained by an electrolytic process of reduction.

H. W.

### **The Question of the Existence of Zirconium Monoxide.**

ROBERT SCHWARZ and HUGO DEISLER (*Ber.*, 1919, **52**, [B], 1896—1903).—Winkler (A., 1890, 1375), Dennis and Spencer (A., 1896, ii, 558), and Wedekind (A., 1905, ii, 596) have studied the reduction of zirconium dioxide by magnesium, and obtained black powders which recombined with oxygen on heating in the air, the increase in weight approximating to that required by the formula  $ZrO$ . The experiments have been repeated under various conditions (in a Rose crucible, in a combustion tube in an atmosphere of carbon dioxide, in porcelain tubes at  $1000^{\circ}$  filled with carbon dioxide or hydrogen or evacuated, and in a crucible fired by thermite), but it is found that it is quite accidental that the black powder left after removing the excess of magnesium and its oxide should increase by the theoretical quantity (nearly 15%) on heating in oxygen. In fact, the more quickly the reduction is performed, the greater is this subsequent absorption of oxygen, rising in one case to 28%.

It appears, therefore, that the black powder is a mixture of metallic zirconium and its dioxide. To test this assumption, various specimens of the powder were heated at about  $250^{\circ}$  in a stream of chlorine or at high temperatures in hydrogen chloride gas, the sublimate being analysed. It was expected that the free metal would give the tetrachloride, the dioxide remain unattacked, and the monoxide, if any, produce water in the case of hydrogen chloride. No indication whatever could be obtained of the presence of the monoxide. The sublimate consisted of the tetrachloride, and its weight agreed exactly with the increase of weight suffered by the powder when heated in oxygen. The dioxide is not attacked at all, even at  $500^{\circ}$ .

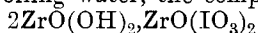
J. C. W.

### **Zirconyl Compounds with the Oxy-halogen Acids.** F. P.

VENABLE and I. W. SMITHEY (*J. Amer. Chem. Soc.*, 1919, **41**, 1722—1727).—Zirconium hydroxide does not dissolve in iodic acid, and therefore zirconium iodate was prepared by adding iodic acid solution to a solution of zirconyl chloride, when a white precipitate,



insoluble in water, alcohol, and ether, was obtained. It was decomposed by hydrochloric acid, with evolution of chlorine, and at  $125^{\circ}$  iodine was evolved. The precipitate was filtered without any washing, and other samples were filtered and washed with measured volumes of water with the object of determining the amount of hydrolysis. The unwashed precipitate had the composition  $\text{ZrO}(\text{OH})_2, 2\text{ZrO}(\text{IO}_3)_2$  when obtained from concentrated solutions, but from dilute solutions the salt is more basic and has the composition  $5\text{ZrO}(\text{OH})_2, 8\text{ZrO}(\text{IO}_3)_2$ . When the second compound was washed with 6 litres of water at the ordinary temperature, the compound had the composition  $3\text{ZrO}(\text{OH})_2, 4\text{ZrO}(\text{IO}_3)_2$ . On washing with 20 litres of boiling water, the compound



was obtained, and with 30 litres of boiling water the compound  $3\text{ZrO}(\text{OH})_2, \text{ZrO}(\text{IO}_3)_2$  was produced. Zirconium hydroxide is readily soluble in 30% perchloric acid. When the action was allowed to take place at the ordinary temperatures, the compound  $\text{ZrO}(\text{ClO}_4)_2, \text{HClO}_4$  crystallised out in large, triclinic crystals, but when perchloric acid was heated with an excess of zirconium hydroxide, the compound  $\text{ZrO}(\text{OH})_2, 9\text{ZrO}(\text{ClO}_4)_2$  was obtained in crystal clusters, which were soluble in alcohol, ether, benzene, chloroform, or carbon tetrachloride, but could not be recrystallised from these solvents. On adding potassium chlorate to a cold concentrated solution of zirconyl perchlorate, crystals of basic zirconyl chlorate,  $\text{ZrO}(\text{OH})_2, 3\text{ZrO}(\text{ClO}_3)_2$ , were obtained. The crystals were extremely deliquescent, very soluble in alcohol, but insoluble in ether. They were faintly yellow in colour, had an odour of chlorine dioxide, and oxidised organic matter very readily.

J. F. S.

### **Elimination of Vanadium from the Arsenical Waters of the Bellville District, Province of Córdoba, Argentine.**

FREDERICO REICHERT and RAUL WERNICKE (*Anal. Soc. Quim. Argentina*, 1919, **7**, 110—113).—Solutions of ferric salts and of ferrous sulphate added in small quantities to alkaline solutions of sodium vanadate cause the precipitation of the vanadium as insoluble ferric vanadate, and also by adsorption on the ferric hydroxide formed. It is proposed to apply the method for the simultaneous removal of arsenic and vanadium from natural waters.

W. S. M.

[**Preparation of Potassium Pyroantimonate for the Estimation of Sodium.**] J. D. VAN LEEUWEN (*Chem. Weekblad*, 1919, **16**, 1426).—Potassium pyroantimonate, which will remain unaffected for a prolonged period, is made as follows: 20 grams of potassium antimonyl tartrate are mixed with an equal quantity of potassium nitrate, and the mixture is heated to redness in a crucible. When reaction has ceased, the lid is placed on the crucible, and heating continued for fifteen minutes. After cooling, 50 c.c. of warm water are added, and the mass stirred until it

becomes powdery. It is then filtered through a porcelain vacuum filter, the residue is treated with 100 c.c. of cold water, and transferred with the filter paper to a flask containing 500 c.c. of boiling water. After boiling for one minute and rapidly cooling, some aluminium hydroxide is added, the mixture is shaken, and finally passed through an ordinary filter paper. W. J. W.

**Bismuth Thiosulphate Compounds.** L. VANINO and F. MUSSGNUM (*Arch. Pharm.*, 1919, **257**, 264—266).—The authors have prepared various double thiosulphates of bismuth by making use of bismuth-mannitol solution. Hauser (A., 1903, ii, 487) describes an unstable bismuth sodium thiosulphate, but a stable compound,  $\text{BiNa}_2(\text{S}_2\text{O}_3)_3$ , which crystallises in small octahedra, is obtainable by the interaction of bismuth-mannitol solution and sodium thiosulphate in presence of manganese chloride. *Bismuth ammonium thiosulphate*,  $\text{Bi}(\text{NH}_4)_3(\text{S}_2\text{O}_3)_3 \cdot 2\text{H}_2\text{O}$ , forms a yellow precipitate, which soon changes colour, and on solution in water undergoes decomposition. *Bismuth strontium thiosulphate*,  $\text{Sr}_3[\text{Bi}(\text{S}_2\text{O}_3)_3]_2$ ,

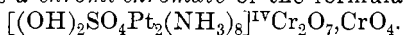
prepared from bismuth-mannitol solution and strontium thiosulphate, forms a yellow, indistinctly crystalline mass, and undergoes hydrolysis when dissolved in water. The bismuth-silver compound, similarly obtained, forms a yellow precipitate, becoming black in a few seconds; the bismuth-copper compound is precipitated only on addition of alcohol.

Unsuccessful attempts were made to prepare bismuth dithionate and trithionate. On addition of sodium trithionate (compare Willstätter, A., 1903, ii, 543) to bismuth-mannitol solution, the liquid soon blackens; as this behaviour is not shown by sodium dithionate, the presence of bivalent sulphur in trithionic acid is proved. T. H. P.

**Platotriammine Sulphite.** D. STRÖMHOLM (*Zeitsch. anorg. Chem.*, 1919, **108**, 211—214).—When the ammonium salt of trichloroplatosulphonic acid is warmed in aqueous solution with excess of ammonia, *platotriammine sulphite*,  $\text{Pt}(\text{NH}_3)_3\text{SO}_3$ , is formed as a sparingly soluble, white, microcrystalline powder. It seems to be identical with the substance which was described by Birnbaum (*Annalen*, 1869, **76**, 142) as platotetrammine sulphite. When its hydrochloric acid solution is oxidised with chromic acid, the diammine,  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ , is formed. Solubility determinations showed that only the *trans*-isomeride was formed. This conclusion was confirmed by the preparation of the oxalate, which is quite distinct from that given by the *cis*-compound. E. H. R.

**Platinitetrammine Disulphite.** D. STRÖMHOLM (*Zeitsch. anorg. Chem.*, 1919, **108**, 184—190).—To determine definitely whether the compound prepared by Cleve by the action of sulphurous acid on Gros's nitrate,  $\text{PtCl}_2(\text{NH}_3)_4(\text{NO}_3)_2$ , contains bi- or quadri-valent platinum, a study of its formation, reduction,

and oxidation has been made, with the result that the compound has been proved to have the composition  $\text{Pt}(\text{NH}_3)_4(\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$ . The yield of the disulphite obtained from the nitrate is only about 66% of the theoretical, and a certain amount of sulphuric acid is formed during the reaction, but not so much as would be required to be formed if the platinum were reduced from the quadrivalent to the bivalent condition. When the compound is oxidised by means of chromic acid, the oxygen used is all accounted for by the oxidation of the sulphurous acid to sulphuric acid, that is to say, there is no oxidation of the platinum. The product of the chromic acid oxidation is a *chromi-chromate* of the formula



By prolonged heating with dilute sulphuric acid, this compound is transformed into the salt,  $[(\text{OH})(\text{SO}_4)\text{Pt}(\text{NH}_3)_4]\text{Cr}_2\text{O}_7$ , previously prepared by Cleve. The same two chromates were prepared from Rajewski's nitrate,  $[(\text{OH})\text{ClPt}(\text{NH}_3)_4](\text{NO}_3)_2$ .

When the platinitetrammine disulphite is boiled with water or heated with acids, platinotetrammine sulphate is formed, the quadrivalent platinum being reduced by half the sulphurous acid, which becomes oxidised to sulphuric acid, whilst the other half of the sulphurous acid escapes. The same reaction takes place incompletely when the salt itself is heated.

E. H. R.

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## Mineralogical Chemistry.

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**The Genesis of Petroleum as Revealed by its Nitrogen Constituents.** CHARLES F. MABERY (*J. Amer. Chem. Soc.*, 1919, **41**, 1690—1697).—It has already been shown that the heavier varieties of petroleum in the California, Texas, Ohio, Canada, Russian, and similar fields are complex mixtures of the denser hydrocarbons with oxygen, sulphur, and nitrogen derivatives. They all differ widely in composition from the lighter varieties in the eastern territory. An examination of twenty-one specimens of the latter, however, discloses in every case the presence of nitrogen in amount varying from 0.01 to 0.48%, so that the conclusion is justified that nitrogen is contained in the petroleum of all the principal oil fields in forms of combination which could have had their origin only in the remains of vegetable or animal bodies. Presumptive evidence has been shown that the associated hydrocarbons in petroleum had the same origin.

Nitrogen is estimated by Kjeldahl's method on the one hand and by a process which is a combination of the Dumas procedure for nitrogen and the oxygen combustion for carbon on the other. For details of the latter and of the special precautions required in the estimation of such minute proportions of nitrogen in oils, the

original paper must be consulted. The results obtained by the two methods show very fair agreement.

H. W.

**Probable Identity of Peganite with Variscite.** LORENZO MOSCHETTI (*Atti R. Accad. Sci. Torino*, 1917—1918, **53**, 652—656).—The author has analysed and examined physically Breithaupt's peganite (*J. Chem. Physik*, 1830, **60**, 308), his results indicating the identity of this mineral with variscite. The composition given by Hermann (*J. pr. Chem.*, 1844, **33**, 287) for peganite is erroneous.

T. H. P.

**Identity of Spangite with Phillipsite.** F. ZAMBONINI (*Atti R. Accad. Sci. Torino*, 1917—1918, **53**, 47—54).—The spangite described by Mantovani (private communication, 1872) is found to be devoid of magnesium, and its crystallographic characters show that it is identical with the phillipsite of the leucitites found in the neighbourhood of Rome.

T. H. P.

**The Minerals of the Valley of Gava in the Voltri Group ; a New Variety of Talc.** EMILIO REPOSSI (*Atti Soc. Ital. Sci. Nat.*, 1918, **57**, 131—155).—The geology of the region is outlined and a number of minerals described. Crystallography or other features are given of garnet, vesuvianite, diopside, hornblende, chlorite, titanite, apatite, pyrite, magnetite, ilmenite, and calcite. Many of these are coated with a mineral, which seems to be a new variety of talc, and is named *gavite*, after the locality. Its properties are: colour, milk-white, yellow, or green, sometimes the colour of nickel salts; lustre in mass, velvety, on surfaces of individual blades, pearly; structure, thin crusts with mammillary surface, made up of bunches of flakes. Microscopic study shows aggregate polarisation, with the optical properties: elongation, +; extinction, parallel; interference colours, brilliant;  $n$  1.544 and 1.582 by immersion method, about, double refraction thus 0.038; in all these properties it is similar to talc. It is infusible before the blowpipe, responds to tests for magnesium and silica, and is somewhat readily soluble in hydrochloric acid. Analysis gave:

SiO <sub>2</sub> .	MgO.	Fe <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O at 110°.	H <sub>2</sub> O above 110°	Total.
59.20	28.57	3.23	1.45	6.61	99.06

The water is expelled in two definite stages, in the amounts stated. Disregarding the water below 110°, the revised percentages correspond with the formula  $H_4(Mg,Fe)_4Si_5O_{16}$ . Gavite differs from talc in the high content of water and in its solubility in acid.

CHEMICAL ABSTRACTS.

**The Oxidation of Lava by Steam.** J. B. FERGUSON (*J. Washington Acad. Sci.*, 1919, **9**, 539—546).—It is generally supposed that water vapour in volcanic gases would have an oxidising action on any ferrous iron present in the lava. Fresh Kilauean lava has been shown to contain 9.28% ferrous oxide and 1.92% ferric

oxide, and this fact might be used as an argument against the presence of a preponderance of water vapour in the gases. Very little is known, however, of the action of steam on silicate minerals containing ferrous iron, and a number of experiments are here recorded in which ground Kilauean lava was exposed to the action of water vapour in an atmosphere of nitrogen at  $1000^{\circ}$ . As a result of the heating, there was found a slight decrease in the ferrous iron content of the rock, but this occurred both in presence and absence of steam, which behaved as an inert gas. The experiments leave no doubt that a considerable amount of ferrous iron, when in silicate combinations, can exist in the presence of water vapour at high temperatures. When a sample of the lava was heated strongly in air for two hours, the ferrous iron content fell to 1.94%, but on again heating in a partial vacuum for four hours at  $1100^{\circ}$ , it rose again to 3.9%. The bearing of these experiments on the interpretation of results obtained by pumping gases from rocks at high temperatures is emphasised.

E. H. R.

**Cumberland Falls Meteorite.** ARTHUR M. MILLER (*Science*, 1919, **49**, 541—542).—This meteorite was seen at midday on April 9th, 1919, passing over north-eastern Tennessee in a course N. 30 W., its progress being noted and in some instances timed by telegraph and telephone operators. It reached the earth in south-eastern Kentucky, striking with earthquake violence. At the time of writing, seven pieces, ranging from 360 to 2378 grams, have been found, and their covering of glaze indicates that the splitting off from the main mass occurred at a considerable distance from the ground. Fifty-two pieces, weighing from less than 30 grams up to 1800 grams, have been found that are parts of a mass weighing originally about 14 kilos. A chemical examination by ALFRED PETER shows the mineral to be mainly enstatite, through which is disseminated particles of nickel-iron and iron sulphides. D 3.18.

CHEMICAL ABSTRACTS.

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### Analytical Chemistry.

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**The Process of Preparation of Charcoal Sticks for Reduction.** NESTOR C. ALEXANDRESCU (*Bull. Soc. chim. România*, 1919, 1, 11—12).—The following process for the preparation of charcoal sticks for the reduction test in qualitative analysis is advocated. Thin wood chips, such as are used in match making, are boiled for two minutes in a 2.5% solution of ammonium phosphate, and then dried at a temperature not exceeding 60°. When it is required to carry out the test, half the stick is burnt, and then the test is carried out in the usual manner on the substance previously mixed with sodium carbonate. W. G.

**Titration with Surface-active Substances as Indicators. Estimations of Acidity with the Homologues of the Fatty Acids Series.** WILHELM WINDISCH and WALTHER DIETRICH (*Biochem. Zeitsch.*, 1919, **97**, 135—156).—Adopting Traube and Somogyi's method (A., 1915, ii, 101) of estimating the reaction by means of the alteration in the surface tension brought about by the displacement of the acid or the base of the indicator by the acid or base of the medium, the authors tried the homologues of the salts of the fatty acids series up to undecylic acid as indicators. The acids with  $C_9$ — $C_{11}$  have been found to be as sensitive as litmus and neutral-red. Free acids can be estimated in the presence of a primary phosphate by using the above acids as indicators.

S. S. Z.

**A Considerable Source of Error in Titrations in the Presence of Phenolphthalein.** HAEÜSSERMANN (*Süddentech. Apoth. Zeit.*, 1919, **59**, 361—362; from *Chem. Zentr.*, 1919, iv, 396).—The author directs attention to the errors, caused by the presence of free carbon dioxide in distilled water, which occur in titrations in which phenolphthalein is used as indicator. H. W.

**Preparation of Phenolphthalein Solution and Paper without the Use of Alcohol.** H. CLAASSEN (*Zentr. Zuckerind.*, **26**, 209; *Arch. Suikerind.*, 1919, **26**, 1588—1590).—When alcohol is unavailable, an indicator solution may be prepared by dissolving 1 gram of phenolphthalein in 12.5 c.c. of *N*-sodium hydroxide, and diluting to 500 c.c. with water. The alkali content of the solution is so small that it can be disregarded in factory work. Where greater accuracy is required, the result can be corrected for the alkalinity of the indicator. Test paper can be prepared by immersing paper first in a solution made by diluting 200 c.c. of the above indicator solution to 1 litre, drying, immersing it in a solution of sulphuric acid of the proper strength to give the desired acidity, and drying again. The results obtained with the paper should be verified from time to time by direct titration.

CHEMICAL ABSTRACTS.

**Estimation of Bromine in Mineral Waters and Brines.** W. F. BAUGHMAN and W. W. SKINNER (*J. Ind. Eng. Chem.*, 1919, **11**, 954—959).—Chromic acid liberates bromine from bromides quantitatively at the ordinary temperature, and the bromine may be removed by aspiration. Chlorides under the same conditions yield only a trace of chlorine, which probably forms chromyl chloride and remains in solution. When a mixture of chlorides and bromides is treated with the reagent, some chlorobromide is formed, and is removed, together with the bromine, on aspiration. In the method of analysis described, the residue from the mineral water is oxidised with chromic acid, with the addition of hydrogen peroxide, and the liberated halogens absorbed in a solution of sodium sulphite and carbonate. This is evaporated, and the residue



again oxidised with chromic acid, and a current of air aspirated through the apparatus, the absorption vessels of which contain potassium iodide solution. In this second aspiration the quantity of chlorine present is so small that only pure bromine is evolved, and its amount is found by titration of the liberated iodine. [See also *J. Soc. Chem. Ind.*, 1920, 19A.] C. A. M.

**Test Paper for the Detection of Iodine.** ANONYMOUS (*J. Pharm. Belg.*, 1919; from *Ann. Chim. anal.*, 1919, [ii], 1, 357).—One gram of starch is mixed with 10 c.c. of water, 40 c.c. of boiling water are added, the mixture is boiled for two minutes, and 0.5 gram of sodium nitrite is then added. The paste obtained is painted on strips of paper by means of a brush, and the strips are dried. To make the test, a few drops of the solution under examination are poured on the paper, followed by one drop of dilute sulphuric acid. A blue coloration is obtained if the solution contains iodide. The test paper keeps well. W. P. S.

**The Spectrocomparator, an Apparatus for the Estimation of the Percentage Saturation of Blood with Oxygen or Carbon Monoxide.** AUGUST KROGH (*J. Physiol.*, 1919, 52, 281—287; from *Chem. Zentr.*, 1919, iv, 210—211).—A modification of Hartridge's method (A., 1912, ii, 488) is proposed which gives satisfactory results and only requires small amounts of blood. The apparatus is fully described and figured in the original, which must be consulted for details. H. W.

**Method for bringing Elementary Sulphur into Solution for Analysis.** A. P. BJERREGAARD (*J. Ind. Eng. Chem.*, 1919, 11, 1055).—The finely divided sulphur is dissolved in a small quantity of dry bromine, nitric acid is added, and the mixture heated. The oxidation requires a few minutes only; after the excess of bromine has been expelled, the mixture is diluted with water, boiled with the addition of hydrochloric acid to expel nitric acid, and the sulphuric acid is then precipitated in the usual way as barium sulphate. W. P. S.

**Non-protein Sulphur of the Blood.** M. KAHN (*Proc. Soc. Exp. Biol. Med.*, 1919, 16, 139; from *Physiol. Abstr.*, 1919, 4, 374).—A method of fractionating and estimating the non-protein sulphur of the blood is described. J. C. D.

**The Titration of Sodium Thiosulphate Solutions.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, 56, 644—657).—The preparation, testing, and application of various substances for the standardisation of thiosulphate solutions are described in detail, and their relative merits for the purpose discussed. The purest forms of potassium dichromate obtainable commercially contain free chromic acid or potassium chromate. A method for the detection and estimation of these is given which depends on the location of a discontinuity in the conductivity curve on the addition of alkali or acid.

If chromic acid is present the addition of standard alkali causes no increase in the conductivity of a dichromate solution until the free acid is neutralised. Similarly, no increase in conductivity is observed on the addition of acid to a solution containing chromate until all the latter has been converted into dichromate. For analytical purposes it is recommended to melt the pure dichromate in an electric furnace before use. The other substances examined are iodine, oxalic acid, cyanogen iodide, potassium iodate, and potassium bromate. All these are easily purified, and give results in the titration of thiosulphate with an error of less than 0.1%. The greatest error, 0.07%, was observed in titrating with dichromate.

W. S. M.

**Influence of the Position of Substituents on the Behaviour of Aromatic Nitro-compounds in the Kjeldahl Estimation of Nitrogen.** B. M. MARGOSCHES and ERWIN VOGEL (*Ber.*, 1919, 52, [B], 1992—1998).—The behaviour of the isomeric nitrophenols, nitrobenzoic acids, and nitrobenzaldehydes when treated with sulphuric acid and potassium sulphate has been investigated; it is found that the nitrogen content of the ortho-derivatives can be correctly estimated in this manner, but that the results for the meta- and para-derivatives are much too low. The favourable action of the hydroxy- or alkoxo-group in the ortho-position to the nitro-group is further shown by the fact that the process gives exact results with 2-nitroresorcinol, 3-nitro-*p*-cresol, and *o*-nitrophenetole, but low results with *p*-nitrophenetole. A further series of experiments shows that the presence of *o*-nitrophenol or of *o*-nitrobenzoic acid has a favourable influence on the behaviour of the corresponding meta- and para-derivatives, and that this action cannot be ascribed solely to their content of phenol or benzoic acid. The possibility that condensation products of the *o*-nitro-compounds may be the active agents has led to an investigation of the behaviour of phthalic acid, phthalic anhydride, and phenolphthalein under like conditions, but the expected favourable action was not observed. The use of salicylic acid appears particularly advantageous in the case of meta-compounds. It is somewhat remarkable that the three isomeric nitrocinnamic acids yield accurate results.

A further series of determinations is recorded with 2:4-dinitrophenol, 2:4-dinitro- $\alpha$ -naphthol, 2:4-dinitrobenzoic acid, 2:4-dinitrotoluene, 3:5-dinitrobenzoic acid, 2:6-dinitrotoluene, and 2:4:6-trinitrophenol; the results are considerably too low in every case, although concordant among themselves. The facts, however, that the 2:4-dinitro-compounds give higher values than the corresponding 3:5- or 2:6-dinitro-derivatives, and that 2:4-dinitrophenol gives results almost identical with those obtained with 2:4-dinitrotoluene, are in accordance with the observations made with the mononitro-compounds.

H. W.

**Grete's Volumetric Method (for Estimating Phosphoric Acid).** R. W. TUINZING (*Landw. Versuchs.-stat.*, 1919, 94, 191—195. Compare A., 1916, ii, 490).—This method was found

to be trustworthy. Directions are given for the preparation of the ammonium molybdate-gelatin solution used, and for the recovery of ammonium molybdate from the residual solutions. W. P. S.

**Behaviour of certain Organic Arsenic Compounds in Marsh's Test.** DOMENICO GANASSINI (*Boll. Chim. Farm.*, 1919, **58**, 385—390).—The addition of platinum chloride to promote the evolution of hydrogen is inadvisable, even in the case of mineral arsenic, since it may fix part of the arsenic as platinum arsenide. In the case of cacodylic acid, platinum chloride in large excess combines to form a double compound, cacodylplatinochloride, which may remain undecomposed. An analogous compound is formed between platinum chloride and methylarsinic acid. Cacodylic acid, in Marsh's test, produces an orange-yellow deposit in addition to the ordinary black deposit. This probably consists of erythrarsine. By heating the hydrogen flask to about  $335^{\circ}$  in a bath of melted lead only the orange-yellow deposit is obtained. Methylarsinic acid and neosalvarsan under the same conditions also yield yellow deposits, but these may be distinguished from the cacodylic acid deposit by the fact that during the formation of the former the gas does not form dense, white fumes. The gas from the methylarsinic acid test gives a yellow precipitate with Bettendorf's reagent (stannous chloride solution saturated with hydrogen chloride), whilst the lemon-yellow ring from neosalvarsan is only formed at a high temperature, does not change to black, and is readily soluble in ammonia solution. Atoxyl and salvarsan yield only the ordinary black rings in the test. [See also *J. Soc. Chem. Ind.*, 1920, 42A.]

C. A. M.

**Separations in the Arsenic Group.** WILHELM STRECKER and ADOLF RIEDEMANN (*Ber.*, 1919, **52**, [B], 1935—1947).—The authors recommend the following modification of the distillation method for the estimation of arsenic. The arsenic solution is placed in a flask provided with a dropping funnel and connected through an efficient worm condenser with a vessel containing water; the flask is half filled with concentrated hydrochloric acid, potassium bromide (1.5 grams), and a few pieces of porous earthenware are added. The contents of the flask are heated to gentle boiling, and thionyl chloride (10 c.c.) is gradually run in at such a rate that the time of addition is half an hour. The distillate is diluted with water to 700—800 c.c., boiled under reflux in a brisk current of carbon dioxide until sulphur dioxide is completely expelled, and the sulphur has collected (this should be the case in half an hour at the most), and filtered. Arsenic is estimated in the filtrate as the trisulphide. Phosphorus trichloride (25 c.c.) may replace the thionyl chloride, in which case the subsequent boiling of the distillate is unnecessary; on the other hand, the presence of phosphorous acid in the residue often causes complications in subsequent estimations. The method gives accurate results, and can be applied to the separation of arsenic from antimony, tin, copper, lead, mercury,

and iron, and for the estimation of arsenic and iron in arsenide of iron.

The separation of antimony from tin can be effected by taking advantage of the fact that antimony chloride is volatile at  $155\text{--}165^\circ$  from solutions in which the tin can be rendered non-volatile by the presence of phosphoric acid; the tin can be volatilised subsequently at a somewhat higher temperature by taking advantage of the fact that the addition of hydrobromic acid destroys the restraining action of the phosphoric acid. The authors have attempted to shorten the time required for this separation by utilising the catalysing action of hydrobromic acid from the commencement, but the results are unsatisfactory, since tin distils over with the antimony, the catalysing influence of hydrogen bromide outbalancing the restraining effect of phosphoric acid. On the other hand, the use of hydrobromic acid is very advantageous in the separation of antimony or tin alone from other elements, and does not require the absence of nitric acid. Thus, in the separation of antimony and copper, the hydrochloric acid solution of the metals is added to concentrated sulphuric acid (6 c.c.) and phosphoric acid (D 1.78, 7 c.c.) contained in a distillation flask connected with a receiver containing hydrochloric acid. The contents of the flask are heated at  $160^\circ$ , and a mixture of concentrated hydrochloric acid (10 volumes) and hydrobromic acid (D 1.78, 1 volume) is added at such a rate that the temperature remains constant. The antimony is completely removed in thirty minutes. The separation of antimony from lead is accomplished similarly.

Tin is quantitatively separated from copper and lead in an analogous manner; the solution of the metals in concentrated hydrochloric acid is treated with sulphuric acid (12 c.c.) and distilled at  $160^\circ$  with the regulated addition of the hydrochloric-hydrobromic acid mixture (20 c.c.). The process is complete in half an hour; the tin is precipitated from the distillate as the sulphide and weighed as the oxide. The method can be applied to the estimation of tin in brass.

The separation of antimony and tin from mercury cannot be effected in this manner, since the latter is also partly volatilised.

A novel type of filter tube is described which is constructed by drawing out the end of a piece of wide glass tubing so as to form a stem; a filter disc covered with asbestos rests on the shoulder of the wider tube, which is further provided with a ground-in cap in which a capillary opening is made. H. W.

#### **Early Developments in Organic Macro- and Micro-analysis.**

J. V. DUBSKÝ (*Chem. Weekblad*, 1919, **16**, 1482—1493).—The author gives a retrospect of the work of various experimenters in connexion with the analysis of organic substances, and indicates the lines along which research progressed. W. J. W.

#### **Gas Analytical Combustion with Copper Oxide.**

E. OTT (*J. Gasbeleucht.*, 1919, **62**, 89—90; from *Chem. Zentr.*, 1919, iv, 171—172).—Uncertainties in fractional combustion with copper

oxide arise in consequence of the dissociation,  $\text{CuO} = \text{Cu} + \text{O}$ , which can be eliminated by subsequent, repeated passage of the nitrogen over the material in the quartz tube, which is maintained at a low red heat. Preparation of chemically pure nitrogen by means of phosphorus and heated copper oxide is liable to error, and recourse should be had to the pyrogallol method. Copper oxide does not appear to be suitable for gas analyses in which the carbon dioxide formed by combustion is measured.

H. W.

**Estimation of Carbon Monoxide in Blood.** D. D. VAN SLYKE and H. A. SALVESEN (*Proc. Soc. Exp. Biol. Med.*, 1919, **16**, 140; from *Physiol. Abstr.*, 1919, **4**, 374).—The blood is treated as in the estimation of oxygen by Van Slyke's method. A mixture of carbon monoxide and oxygen with a slight amount of nitrogen is obtained. The oxygen is absorbed by alkaline pyrogallol solution. The residual gas, after a correction has been made for nitrogen, is carbon monoxide.

J. C. D.

**A Micro-method for the Estimation of Calcium in Blood-serum, and other Organic Substances.** D. J. DE WAARD (*Biochem. Zeitsch.*, 1919, **97**, 176—186).—The substances are evaporated and incinerated, and the salts of the ash extracted with dilute hydrochloric acid. The calcium is precipitated from the solution as the oxalate, which is centrifuged, washed, dissolved in dilute acid, and titrated with potassium permanganate. 0.1 Mg. of calcium can be estimated by this method with an error of 4%.

S. S. Z.

**A Direct Micro-estimation of Calcium in the Serum.** D. J. DE WAARD (*Biochem. Zeitsch.*, 1919, **97**, 186—189).—All the calcium can be precipitated directly from the serum by means of ammonium oxalate and be estimated by the method described in the preceding abstract. The difference between an estimation carried out on the incinerated serum and on the original serum was only 0.001 mg. of calcium per c.c.

S. S. Z.

**Ferrous Sulphide as an Indicator in Acidimetry and a New Volumetric Method for the Estimation of Zinc.** J. HOUBEN (*Ber.*, 1919, **52**, [B], 1613—1621).—Since the production of ferrous sulphide is prevented by the slightest traces of acids, it is possible to titrate an acid by adding a crystal of pure ferrous ammonium sulphate, passing in well-washed hydrogen sulphide (not enough to saturate the solution), and running in alkali until the black colour of ferrous sulphide is permanent. Experiments with hydrochloric and sulphuric acids on the one hand and alkali hydroxides and carbonates or borax on the other show that the end-point is quite as definite as it is in the case of methyl-orange or phenolphthalein. The only indistinct end-point is found when titrating sulphuric acid with borax, but here the difficulty may be overcome by running in more acid until the black colour just disappears again. The method is obviously useful in the case of coloured liquids, or when working in a bad light.

In the case of zinc salts, hydrogen sulphide completely precipitates zinc as sulphide from the sulphate if the solution is less than 0.2*N*, and from the chloride if the concentration is below 0.067*N*. A titration of the free acid produced would therefore be a means of estimating zinc in its neutral salts, and here the above use of a ferrous salt proves its worth. The solution is saturated with hydrogen sulphide, some ferrous ammonium sulphate is added, and alkali is run in, preferably borax solution, until the white turbidity becomes brown. A "back titration" with an acid is not possible in this case, however, without first filtering the zinc sulphide, as a double zinc-ferrous sulphide is formed which is not quickly broken up. Of course, cobalt and nickel salts must be absent.

Examples of the application of the method to metallic zinc, zinc salts, zinc ash, and blende show that the results approach those obtained by gravimetric analysis very closely, in fact much more so than those given by any other volumetric method. Blende is examined as follows. About 5 grams of the mineral are digested with 40 c.c. of concentrated hydrochloric acid and 40 c.c. of water, the solution filtered and saturated with hydrogen sulphide, filtered again, and diluted to 1000 c.c. with dilute hydrochloric acid. Portions of 50 c.c. are now neutralised with sodium carbonate, using methyl-orange, treated with hydrogen sulphide for half an hour, mixed with ferrous ammonium sulphate, and titrated with borax or sodium carbonate.

The alkalimetric titration of ferric salts may be carried out by employing the same principles.

J. C. W.

### **Electrometric Analysis with Potassium Ferrocyanide.**

ERICH MÜLLER (*Zeitsch. angew. Chem.*, 1919, **32**, 351—352).—Electrometric titration of lead and zinc salts with potassium ferrocyanide solution is trustworthy, but the method fails in the case of other metals owing to the fact that the precipitates produced do not have definite compositions.

W. P. S.

### **Colorimetric Estimation of Lead Dioxide in Litharge.**

WALLER V. MORGAN (*J. Ind. Eng. Chem.*, 1919, **11**, 1055).—The method depends on the fact that lead dioxide oxidises aniline to aniline-purple, and that the coloration obtained is proportional to the amount of the dioxide present. Five grams of the litharge containing lead dioxide are boiled for one minute with 2 grams of aniline hydrochloride dissolved in 10 c.c. of water and 5 c.c. of concentrated hydrochloric acid; the mixture is then filtered and the coloration exhibited by the filtrate compared with those given under the same conditions by litharge containing known amounts of lead peroxide.

W. P. S.

### **Complex Internal Salts in Quantitative Analysis. I.**

I. BELLUCCI and A. CHIUCINI (*Gazzetta*, 1919, **49**, ii, 187—216).—The authors summarise and criticise published work on the applications of  $\alpha$ -nitroso- $\beta$ -naphthol and "cupferron" to the separation and estimation of metals.

For the separation of copper, neither of these reagents offers appreciable advantages over ordinary analytical methods, except perhaps for the separation of copper from arsenic and, more particularly, from antimony. For the separation of iron, cupferron is to be preferred to  $\alpha$ -nitroso- $\beta$ -naphthol, chiefly because the ferric precipitate obtained with the former withstands a greater degree of free mineral acidity, and is therefore more easily freed from extraneous metals, and also because the precipitate is less voluminous.  $\alpha$ -Nitroso- $\beta$ -naphthol serves principally as a reagent for cobalt, and also as a reagent for palladium, whilst cupferron acts as a reagent for titanium, zirconium, and vanadium, as well as for iron. The two compounds assume, indeed, the character of general reagents for groups of elements which contain, however, elements quite different from those usually classed together. T. H. P.

**Detection of Cerium.** FR. FEIGL (*Österr. Chem. Zeit.*, [ii], **22**, 124—126; from *Chem. Zentr.*, 1919, iv, 592).—Lecoq's reaction is much more distinctly obtained after the addition of a small quantity of an aluminium salt, but is not applicable in the presence of iron. A vivid blue coloration is obtained when cerium dioxide is moistened with a solution of benzidine in acetic acid; other cerous and ceric compounds, with the exception of cerous fluoride, cerous carbonate, and double sulphates of cerium, behave similarly. The reaction is most sensitive when the solution under investigation is made just alkaline with sodium or potassium hydroxide, heated to boiling, filtered, and the filter paper treated with a drop of benzidine solution; 0.02 mg. of cerium per litre can be thus detected. The other metals which belong to the ammonium sulphide group of the rare earths, with the exception of thallium, do not show the reaction. The absence of other oxidising agents and of manganese, cobalt, thallium, and chromate is essential, since the reaction depends on oxidation. Faintly acid solutions of iron also give the reaction; after previous addition of sodium or potassium hydroxide, a coloration is not observed. In the presence of iron, it is advisable to precipitate cerium as the fluoride and to convert the latter by alkali hydroxide into the hydroxide, since precipitated ferric hydroxide carries down notable amounts of cerium, which are thus removed from the sphere of action. H. W.

**Soil Analysis.** F. MÜNTER (*Landw. Versuchs.-stat.*, 1919, **94**, 181—189).—For the estimation of iron, aluminium, calcium, magnesium, potassium, and phosphoric acid in a soil, it is recommended that 300 grams of the sample be mixed with 900 c.c. of concentrated hydrochloric acid and shaken occasionally during forty-eight hours; the solution is then decanted, filtered, and 300 c.c. of the filtrate are evaporated with the addition of ammonium chloride. The residue obtained is treated with nitric and hydrochloric acids, again evaporated, this operation is repeated, and the final solution in hydrochloric acid is used, after separation of the silica, for the estimation of the above-mentioned constituents. W. P. S.

**Application of Hæmatoxylin to the Detection of Iron in Tissues.** J. MAWAS (*Compt. rend. Soc. Biol.*, 1919, **82**, 155—158; from *Chem. Zentr.*, 1919, iv, 245).—The author considers that the reaction of hæmatoxylin with ferrous ions is to be ascribed to salt formation, and not, as Macallum assumed, to oxidation. The latter's statement that the reaction only occurs with inorganic iron is incorrect, since iron compounds of the albumins, which are not acted on by hydrogen sulphide or ammonium sulphide, but are affected by potassium ferro- or ferri-cyanide, also show this change. The formation of Prussian-blue is a more delicate test for the presence of iron in tissues; nevertheless, the author has obtained useful results with hæmatoxylin, particularly in certain cases of disease of the eye. The affinity of the hæmatoxylin for the chromatin of the nucleus, whereby a similar coloration is developed, is disadvantageous.

H. W.

**Brazilin and its Iron Lakes.** J. MAWAS (*Compt. rend. Soc. Biol.*, 1919, **82**, 158—159; from *Chem. Zentr.*, 1919, iv, 245).—Brazilin is a more sensitive and more rapid reagent than hæmatoxylin (preceding abstract); its aqueous solution, pale red with an orange fluorescence, gives dark brown, insoluble lakes with ferrous salts. In aqueous or alcoholic solution, it colours tissue containing iron dark brown within a few minutes, whilst the nucleus becomes reddish-violet. Differentiation which may be necessary owing to over-colouring is effected with alcohol and chloroform, or, preferably, with alcohol containing 1% of hydrogen chloride. The nucleus becomes practically decolorised, whilst the iron pigment is unaffected; the former again becomes reddish-violet when washed with dilute aqueous alkali.

H. W.

**Iodometric Estimation of Iron.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 1565—1568).—The estimation of ferrous iron by means of iodine with addition of a pyrophosphate gives results which are about 3% too low owing to oxidation of the iodine by dissolved oxygen in the solutions. If sulphuric acid and sodium hydrogen carbonate are added to eliminate the oxygen, the error is reduced to 0.8—1%. A more suitable method which gives accurate results is the following: 25 c.c. of 0.1N-potassium bromate and 10 c.c. of 25% phosphoric acid are added to 10 c.c. of 0.1N-ferrous solution to which a few drops of acid have been added. After remaining for five minutes in a stoppered flask, 5 c.c. of potassium iodide and 2 drops of molybdate solution are added, the iodine being titrated after five minutes with thiosulphate.

The purpose of the phosphoric acid is to combine with the ferric ions and prevent them interacting with the potassium iodide, and the molybdate is added to accelerate the reaction of the bromate and iodide.

W. J. W.

**Volumetric Estimation of Iron.** J. HOUBEN (*Ber.*, 1919, **52**, [B], 2072—2076. Compare this vol., ii, 53).—The process



permits the estimation of ferrous and ferric iron and free mineral acid in a solution.

A portion of the solution is completely reduced by hydrogen sulphide and titrated with *N*-potassium or sodium hydroxide solution until the dark coloration due to the incipient precipitation of ferrous sulphide is observed, which does not disappear after vigorous shaking; the free acid plus one-third of the acid originally combined with the ferric salt is thereby estimated. A second portion of the solution is reduced with sulphur dioxide (air being completely excluded), most of the excess of the latter is removed by boiling, and the cooled solution is titrated with *N*-alkali as before, after being treated with hydrogen sulphide, which completes the removal of sulphur dioxide. The free acid plus two-thirds of the acid originally united to the ferric iron is thus estimated. The difference between the two titrations multiplied by three gives the number of c.c. of *N*-ferric chloride solution originally present. If this number is subtracted from the smaller of the two burette readings, the difference is the number of c.c. of *N*-acid which were uncombined in the solution. The ferrous salt is estimated in the usual manner. Test analyses show the method to have a high degree of accuracy.

H. W.

### **Separation of Iron, Aluminium, Chromium, Glucinum, Titanium, and Zirconium by the Sodium Carbonate Method.**

P. WENGER and J. WUHRMANN (*Ann. Chim. anal.*, 1919, [ii], 1, 337—339).—A method described previously by Wenger and Wunder (A., 1912, ii, 687) may be applied when the mixture contains titanium or zirconium, but not both. After fusion with sodium carbonate, the insoluble iron and zirconium oxides may be treated with hydrochloric acid (1:1), in which the zirconium oxide is insoluble. In the absence of zirconium, iron and titanium may be separated by one of the known methods, even in the presence of glucinum. [See, further, *J. Soc. Chem. Ind.*, 1920, 46A.]

W. P. S.

### **A New Method for the Volumetric Estimation of Nickel.**

JOSEF HOLLUTA (*Monatsh.*, 1919, 40, 281—291).—The process depends on the fact that, when a nickel salt reacts with dimethylglyoxime, acid is liberated, which is estimated by titration with alkali in the presence of phenolphthalein or methyl-red.

The standard *N*/50-solution is prepared by dissolving 4.6400 grams of pure dimethylglyoxime in the requisite quantity of 97% alcohol (300—400 c.c.); 20 c.c. of *N*-potassium hydroxide solution are added with constant shaking, and the solution is diluted to 1000 c.c. with distilled water free from carbon dioxide and filtered after twenty-four hours from any slight precipitate of potassium carbonate. (The alcohol used must be free from aldehyde and neutral in reaction.) The alkali content of the solution is checked by titration with standard acid, using phenolphthalein or methyl-red as indicator. The nickel solution under examination is diluted

to the required extent, and exactly neutralised with  $N/10$ - or  $N/50$ -potassium hydroxide solution. 2—5 C.c. of the standard solution are added, and, after vigorous agitation, the solution is gently warmed, whereby the precipitate is caused to collect, leaving a clear liquor; the standard solution is then gradually added with frequent agitation until the solution acquires a permanent, pale pink coloration. In consequence of the bulky nature of the nickel precipitate, the amount of the metal in the solution should not exceed 0.03 gram.

The method is particularly advantageous in dealing with very small quantities of nickel, and titration can readily be effected with  $N/100$ -solutions if methyl-red is substituted for phenolphthalein as indicator. The results are not affected by the presence of the alkali salts of strong acids. Further details are promised in a subsequent communication.

H. W.

**Iodometric Estimation of the Chromic Acid in Lead Chromate.** MAX GRÖGER (*Zeitsch. anorg. Chem.*, 1919, **108**, 267—272).—The iodometric method of estimating chromic acid has not hitherto been used for lead chromate on account of the impossibility of completely decomposing the chromate by means of dilute sulphuric acid. Dilute hydrochloric acid dissolves lead chromate completely, but hydrochloric acid has a reducing action on chromic acid, with liberation of free chlorine, and has therefore not been used to dissolve lead chromate. It is now found, however, that if the hydrochloric acid is sufficiently dilute, its reducing action is negligible. Experiments showed that when acid of 1.25*N* strength or less was used, in the proportion of 25HCl to 1 mol. of chromate, no reduction took place after boiling the solution for three hours. With stronger hydrochloric acid, the rate of reduction increased rapidly with the concentration of the acid. For carrying out an analysis, about 0.3 gram of lead chromate is dissolved in 50 c.c. of 1.25*N*-hydrochloric acid by gently heating. The solution is cooled, 1 gram of potassium iodide added, allowed to remain for ten minutes, diluted with 100 c.c. of water, and the free iodine titrated with sodium thiosulphate. There is no need to filter off the precipitated lead iodide, as the colour of this does not interfere with the end-point. After the end of the titration, free iodine again appears after a short time. This is due to atmospheric oxidation of hydriodic acid, a reaction which appears to be catalysed by the lead iodide present. The results obtained by this method are generally about 0.5% too high.

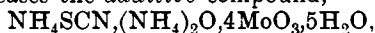
E. H. R.

**Detection of Molybdenum by means of Xanthic Acid.** J. KOPPEL (*Chem. Zeit.*, 1919, **43**, 777—778).—Molybdenum compounds give a characteristic red to plum-coloured reaction with xanthic acid, which was first described by Siewert (*Zeitsch. ges. Naturw.*, 1864, **23**, 5). The test is preferably applied by acidifying the solution with a mineral acid, after the addition of a trace of solid potassium xanthate, and is capable of detecting molybdenum in a solution containing 0.00000064 gram per c.c. The reaction is

weaker when phosphoric, formic, or acetic acid is used for the acidification, and much weaker with salicylic acid, whilst when oxalic, citric, or tartaric acid is used, there is little, if any, coloration. Analogous xanthic compounds are formed by copper, iron, cobalt, nickel, etc., but the colorations do not interfere with the molybdenum test. Vanadic acid forms a yellow compound and uranic acid a brown compound, which, like the molybdenum compound, are soluble in ether and other organic solvents. Tungstic acid, if present in very large preponderance, may interfere with the test. The molybdenum compound may be obtained as a black oil by mixing a solution of 2 grams of ammonium paramolybdate with 1 gram of potassium xanthate. When vigorously stirred, this oil solidifies, forming black crystals with green surface reflections. The mean analyses of Siewert's solid preparation agree with the formula  $\text{MoO}_3(\text{OEt}\cdot\text{C}\cdot\text{S}\cdot\text{S}\cdot\text{H})_2$ . [See also *J. Soc. Chem. Ind.*, 1920, January.]  
C. A. M.

### Colour Reactions of Molybdenum and Tungsten. II.

G. A. BARBIERI (*Atti R. Accad. Lincei*, 1919, [v], 28, i, 390—392. Compare A., 1919, i, 549).—According to Péchard (A., 1894, ii, 319), replacement of the hydrochloric or sulphuric acid used in Braun's reaction by acetic acid results in the formation of a yellow coloration, and, with concentrated solutions, of a yellow, crystalline precipitate, due to conversion of the molybdate into trimolybdate, and union of this with the thiocyanate present to form an additive compound, for instance,  $\text{KCNS}\cdot\text{K}_2\text{O}\cdot 3\text{MoO}_3\cdot 4\text{H}_2\text{O}$ . On repetition of Péchard's reaction with ammonium thiocyanate and ammonium permolybdate or tri- or tetra- or normal molybdate, the author finds that in all cases the *additive* compound,



is formed, and in no case an additive compound of the trimolybdate. From potassium trimolybdate and thiocyanate in presence of acetic acid, the corresponding *compound*,  $\text{KSCN}\cdot\text{K}_2\text{O}\cdot 4\text{MoO}_3\cdot 5\text{H}_2\text{O}$ , is formed; both potassium and ammonium compounds form yellow, acicular crystals.

Ammonium tetramolybdate,  $(\text{NH}_4)_2\text{O}\cdot 4\text{MoO}_3\cdot 2\frac{1}{2}\text{H}_2\text{O}$ , may be obtained by the action of acetic acid on ammonium permolybdate in aqueous solution (compare Junius, A., 1905, ii, 825).

T. H. P.

**Qualitative and Quantitative Test for Molybdenum in Steel and Iron.** SIEGFRIED LAURENS MALOWAN (*Zeitsch. anorg. Chem.*, 1919, 108, 73—80).—A specific and very sensitive test for molybdenum is given by xanthic acid. The test is best carried out with freshly prepared xanthate solution in the following manner. Absolute alcoholic potash is shaken with excess of carbon disulphide until no more of the latter is dissolved. To the solution so obtained, 30% acetic acid is added until it shows a slight yellow turbidity, and the reagent is added drop by drop to the solution to be tested. If molybdenum is present, an intense red colour

develops, which is quite stable in water, and the intensity of which is proportional to the quantity of molybdenum present. The sensitiveness of the reaction is such that 0.000005 gram of molybdenum in 0.0007% solution can be detected with certainty in presence of other elements. The coloured product is readily soluble in ethyl or amyl alcohol, ether, or chloroform, less easily in petroleum and benzene. It is readily extracted from its reddish-violet ethereal solution by alkalis, from which acids precipitate it. The ethereal solution decomposes on keeping, with formation of molybdenum sulphide. The reaction is not given by vanadium, tungsten, titanium, or uranium; chromates give a dark coloration with xanthic acid, and should be reduced, if present, before the test is made. The reaction can be used for the colorimetric estimation of molybdenum, the coloured product being extracted with a mixture of 65% ether and 35% light petroleum, and a mixture of 30% ether and 70% light petroleum used for dilution for comparison with the standard solution. If pure ether is used, decomposition takes place too rapidly for accurate determinations to be made. E. H. R.

**Colorimetric Method for the Estimation of Small Quantities of Uranium.** MÜLLER (*Chem. Zeit.*, 1919, **43**, 739—740).—The method depends on the red coloration obtained when a uranyl salt is treated with sodium salicylate; the coloration yielded by any uranyl salt solution is compared with that produced by a known amount of uranium under the same conditions. Free mineral acid, acetic acid, iron, alcohol, or acetone must not be present, but neutral alkali salts do not interfere. The method is suitable for the estimation of uranium in solutions containing as little as 0.02% of the metal. W. P. S.

**Estimation of Zirconium by the Phosphate Method.** G. E. F. LUNDELL and H. B. KNOWLES (*J. Amer. Chem. Soc.*, 1919, **41**, 1801—1808).—Zirconium can be quantitatively precipitated as secondary zirconium phosphate in cold or tepid solutions containing from 2% to 20% by weight of sulphuric acid, provided that a ten- to one hundred-fold excess of the precipitant, diammonium hydrogen phosphate, is used. Hydrolysis, which occurs when the phosphate precipitate is washed with water, can be almost entirely avoided by the use of a cold 5% ammonium nitrate solution for washing. Zirconium pyrophosphate, for which the  $\text{ZrO}_2$  factor is 0.4632, is obtained on ignition of a secondary zirconium phosphate which has been washed with ammonium nitrate solution. No definite composition can be ascribed to the compound resulting when secondary zirconium phosphate which has been washed with water is ignited. Zirconium can be quantitatively separated as phosphate in a 20% sulphuric acid solution from iron, aluminium, chromium, cerium, and thorium. The separation from titanium can also be effected provided hydrogen peroxide is present. J. F. S.

**Gas-analytical Separation of Acetylene, Ethylene, and Benzene.** W. D. TREADWELL and F. A. TAUBER (*Helv. Chim. Acta*, 1919, **2**, 601—607).—The quantitative absorption of acetylene from mixtures containing it, together with ethylene and benzene vapour, is conveniently effected with a solution of mercuric cyanide (20 grams) in 2*N*-sodium hydroxide solution (100 c.c.); the gas is shaken with the mixture (5 c.c.) for one to two minutes, at the end of which the acetylene is completely absorbed, whilst ethylene and benzene vapour are unaffected.

A solution of mercuric nitrate (20 grams) in 2*N*-nitric acid (100 c.c.) which has been saturated with sodium nitrate is recommended for the absorption of ethylene in the presence of benzene vapour; the gas is shaken with 5—10 c.c. of the solution for two to three minutes. Propylene appears to behave similarly to ethylene, since it is indifferent to alkaline mercuric cyanide solution, whilst readily absorbed by mercuric nitrate solution.

H. W.

**Dehydrogenation of Hydrocarbons by means of Palladium-black.** JENŐ TAUSZ and NIKOLAUS VON PUTNOKY (*Ber.*, 1919, **52**, [B], 1573—1583).—Zelinski has shown that *cyclohexanes* are converted into benzene hydrocarbons by exposing them to the action of palladium-black at 300°, whereas hexane and *cyclopentanes* are unchanged (*A.*, 1913, i, 167). This seemed to offer a process whereby *cyclohexanes* could be estimated in the presence of paraffins, and a method has now been developed which gives satisfactory results within certain limits.

The first difficulty to be overcome was the preparation of a sufficiently active catalyst, for Zelinski's agent is spoilt by mixtures of paraffins and *cyclohexane* long before the latter is completely dehydrogenated. In the reduction of palladium solutions, it is usual to employ formic acid, any excess being destroyed by the palladium-black itself. It seemed possible, therefore, that the activity of the catalyst would suffer in such a treatment, and as it was found, that the activity towards formic acid is parallel to the activity towards *cyclohexane*, it was decided to use no more than the theoretical quantity of the reducing agent. This has the desired effect, the catalyst being much more active. For example, two specimens of 1 gram each, prepared by Zelinski's method, produced 1.8 and 11.2 c.c. of gas from formic acid, but ten samples made by the new process, which is described in detail, gave on an average 458 c.c., one portion developing as much as 840 c.c.

With such an active catalyst, the quantitative dehydrogenation of *cyclohexane* in various mixtures with hexane may be easily realised; but then another disturbing factor appears, namely, that at 300° the saturated paraffins themselves are to a certain extent converted into unsaturated hydrocarbons by palladium black. The small amount of hydrogen set free by the paraffins, however, reaches a constant volume after an hour or two, and although a little more gas is liberated when the catalyst is renewed, an equilibrium

is soon established. A similar equilibrium is reached when the olefines are heated with an excess of hydrogen, that is, the hydrogenation is never quite complete. The volume of hydrogen produced by the paraffins is relatively small compared with the yield from the *cyclohexanes*, so, within certain limits, the proportion of the latter hydrocarbons in a mixture can be gauged from the amount of hydrogen liberated. The limit is generally about 1% of cyclic hydrocarbon, but in some experiments it was as low as 0.5%. For mixtures containing less than this, only the chemical proof of the presence of benzene will suffice. The reaction with trioxymethylene and sulphuric acid is recommended.

For quantitative purposes, a special apparatus is described. The catalyst (12 grams) is contained in a tube heated in a simple electric furnace, and the vapour is continually circulated. The volume of oil employed varies from 10 c.c. for rich mixtures to 100 c.c. In the experiments described, the following volumes of hydrogen were produced by 1 c.c. of hydrocarbon at 300° (or 270° in the case of the methyl derivatives): *cyclohexane*, 614 c.c.; *methylcyclohexane*, 618 c.c.; 1:3-dimethyl*cyclohexane*, 504 c.c.; *isopentane*, 38 c.c.; *n-hexane*, 40.8 c.c. (after renewing the catalyst five times); *n-heptane*, 32.5 c.c.; *n-octane*, 36 c.c.

As an important application of the method, the analysis of a sample of hexane, b. p. 69—71°, from American petroleum is recorded. Whereas 30 c.c. of synthetic *n-hexane* gave only 338 c.c. of hydrogen, 30 c.c. of the natural oil yielded 446 c.c. under exactly the same conditions. This corresponds with 2.4% of *cyclohexane* in the sample, and actually 0.5592 gram of pure dinitrobenzene was obtained from the dehydrogenated 30 c.c. of oil.

J. C. W.

### Criteria of the Degree of Purity of Commercial Toluene.

JOHN SCOTT LUMSDEN (T., 1919, 115, 1366—1372).

**Differentiation of Methyl and Ethyl Alcohols.** PANNWITZ (*Pharm. Zentr.-h.*, 1919, 60, 441—442).—Although crystallised copper sulphate is insoluble in ethyl alcohol and dissolves in methyl alcohol to give a blue solution, this test is useless for distinguishing methyl alcohol from ethyl alcohol, owing to the fact that a small quantity of water destroys the blue colour of the methyl alcohol solution. The quantity of added water must be increased to 35% by vol. before the blue colour reappears, and at this dilution ethyl alcohol also begins to dissolve copper sulphate. The same effects are noticed when ferrous sulphate is used in place of copper sulphate. The borax flame test for methyl alcohol also fails when water is present.

W. P. S.

**Influence of the Presence of Trimethylene Glycol on the Estimation of Glycerol by the Zeisel *iso*Propyl Iodide Method.** C. A. ROJAHN (*Ber.*, 1919, 52, [B], 1454—1460).—Although trimethylene glycol produces no silver iodide precipitate when

digested by itself in the Zeisel apparatus at 120—125°, it does so behave when added to glycerol. In fact, the excess of silver iodide corresponds with the amount of *s*-di-iodopropane produced if the quantity of trimethylene glycol is small. As a consequence, Zeisel's method is not applicable to the estimation of fermentation glycerol (the German "protol"-glycerol), for this contains trimethylene glycol.

J. C. W.

**Chromatic Reactions of Formaldehyde with certain Aromatic Compounds.** ARTURO ROSSI (*Boll. Chim. Farm.*, 1919, **58**, 265—270).—Colorations, which are not necessarily distinctive of the aldehyde, are given by formaldehyde in 0.1 or 0.001% aqueous solution, when added to sulphuric acid containing a trace of certain aromatic compounds in solution. Applied as a zone reaction, the following colorations are obtained: *Gallic acid*, a reddish-brown ring, and, on shaking the tube, a green liquid changing to greyish-green. *Tannic acid*, a reddish-brown ring, and a liquid bluish-green at the bottom, but subsequently brownish-red throughout. *Pyrogallol*, a light rose-coloured ring, and liquid. The test is capable of detecting 0.00001% of formaldehyde. *Salicylic acid*, a light rose-coloured ring and solution. *Catechol* and *resorcinol*, various red rings and liquids.  *$\beta$ -Naphthol*, a violet-red ring, and brownish-black liquid with green fluorescence. *Benzonaphthol*, similar colour reactions. *Phenyl salicylate*, carmine-red ring and reddish-yellow liquid, becoming pink on dilution. *Phenolphthalein*, no ring, but an orange liquid changing to carmine-red on shaking. Dilution with water causes a carmine-red precipitate to separate.

C. A. M.

**Estimation of Formaldehyde in Blood.** E. SALKOWSKI (*Biochem. Zeitsch.*, 1919, **97**, 129—135).—The protein of the blood is hydrolysed with gastric juice. The hydrolysed mixture is distilled and *N*/10-iodine added to the distillate. The residual iodine is then titrated with thiosulphate. The formaldehyde found amounted to only 85.73% of the quantity added to the blood.

S. S. Z.

**Estimation of Acetone and Acetoacetic Acid with Autenrieth's Colorimeter.** H. SCHALL (*Münch. med. Woch.*, 1919, **66**, 812—814; from *Chem. Zentr.*, 1919, iv, 562).—Description of the application of Autenrieth's colorimeter to the colorimetric estimation of acetone according to Legal and to the estimation of acetoacetic acid. Gerhardt's iron chloride reaction is suitable for the estimation of considerable concentrations of the latter (above 0.5%), whilst, at greater dilutions, Rimini's ethylenediamine test is used. The former has the advantage of easy manipulation and constancy of colour, whilst the latter is more sensitive and gives a pure tint which, however, rapidly loses in intensity. Empirical solutions of dyes are used as standards. When acetone and acetoacetic acid are present simultaneously, the estimation of acetone requires

the correction of a factor, since acetoacetic acid gives a positive Legal's reaction which is 5.55 as intense as that of acetone.

H. W.

**An Acetoneurometer.** A. ADLER (*Münch. med. Woch.*, 1919, **66**, 722—723; from *Chem. Zentr.*, 1919, iv, 398).—A colorimetric method of estimating acetone is described which is based on Legal's test. A mixture of urine (10 c.c.), sodium hydroxide solution (20%, 1 c.c.), and sodium nitroprusside solution (33%, 0.5 c.c.) is well shaken, and acetic acid (20 drops) is added. The colour is compared with that given by mixing Neutral-red, New-blue, and Diamond-phosphine. Solutions of the dyes of the following concentrations are prepared: Neutral-red, 1:1000; New-blue, 1:1000; Diamond-phosphine D, 1:100. Ten c.c. of the first, 3 c.c. of the second, and 0.6 c.c. of the third solution are mixed with water, 5 c.c. (solution I), and correspond with 0.1% of acetone. Ten c.c. of solution I diluted with an equal volume of water correspond with 0.08% of acetone; 5 c.c. of solution I with 10 c.c. of water are equivalent in colour to 0.05% of acetone; 5 c.c. of solution I with 15 c.c. of water correspond with 0.01% of acetone. Five c.c. of a solution of neutral-red (10 c.c.), new-blue (1 c.c.), and diamond-phosphine (0.1 c.c.) with water (50 c.c.) correspond with 0.005% of acetone. The solutions are placed in tubes similar to those used in the experiment, which are subsequently sealed. The five standards are in practice sufficient for ascertaining the acetone content of a urine. H. W.

**Methylene-blue as a Reagent for the Detection of Sugar in Urine.** F. URZ (*Süddeut. Apoth. Zeit.*, 1919, **59**, 280—281; from *Chem. Zentr.*, 1919, iv, 212—213).—According to the author's observations, urines which contain sugar always give a positive reaction with solutions of methylene-blue, even when Lieber's modification of the test is used. Aqueous solutions of dextrose behave similarly, but sucrose, carbamide, uric acid, and saliva do not give the reaction. Milk behaves similarly to urine containing sugar. Whilst aqueous solutions of hexamethylenetetramine do not react with methylene-blue, the urines of patients to whom the drug has been administered behave similarly to saccharine urines, but do not give a positive result with Fehling's solution or Nylander's reagent. Normal urines, free from sugar, also give a positive reaction with methylene-blue when they have been preserved for some days and are partly decomposed, and this is particularly noticeable if they have been rendered alkaline with potassium hydroxide. Artificial gastric juice and glycuronic acid are also able to decolorise methylene-blue. The substance, therefore, is not a suitable reagent for the detection of sugar in urine. H. W.

**Rapid Method for the Estimation of Sugar in Urine.** OTTO MAYER (*Arch. Hyg.*, 1919, **88**, 184—197; from *Chem. Zentr.*, 1919, iv, 211—212).—The detection of sugar in urine is best carried out by Trommer's test, for the performance of which, as also for Fehling's and Nylander's reactions, practical directions are given.



The estimation of sugar is effected in the following manner: urine (10 c.c.) is placed in a 100 c.c. stoppered measuring cylinder, sodium hydroxide (15%, 10 c.c.) is added, and the solution is diluted to 50 c.c. with water; copper sulphate solution (25 grams per litre) is gradually added with gentle shaking until the precipitate, which denotes the end of the reaction, practically completely redissolves on vigorous agitation, leaving only a just perceptible but permanent turbidity, which slightly increases in course of time. Under these conditions each c.c. of copper sulphate solution corresponds with 0.1% of dextrose. If the urine contains more than 4% of sugar it is preferable to take only 5 c.c., whilst if the content is 0.5—1% 20 c.c. may be measured out. Separation of alkaline earth phosphates from urines which have been treated with alkali and diluted from 2.5 to 10 times occurs only when these are present in exceptional quantity. In this case, since the sensitiveness of the end-point may be greatly reduced, it is advisable to treat 20 c.c. of the urine with 20 c.c. of sodium hydroxide solution, to filter the solution after dilution to 100 c.c., and to perform the titration with 50 c.c. of the clear filtrate.

For the detection of acetone, powdered sodium nitroprusside (0.05—0.1 gram) is shaken with about 10 c.c. of urine, about 1 c.c. of sodium hydroxide (15%) is added to the solution, which is then acidified with acetic acid (30%, 2 c.c.). In this form the test is so sensitive that distillation is only necessary with such urines as are deeply coloured or contain only small amounts of acetone. The most suitable reagent for the detection of acetoacetic acid is a mixture of liquor ferri. sesquichl. (5 c.c.) and sodium chloride solution (1:3, 95 c.c.), the reaction being performed as a ring test. H. W.

**Volumetric Estimation of Sugar in Milk.** J. L. MAYER (*J. Amer. Pharm. Assoc.*, 1919, **8**, 551—553).—Benedict's method for the estimation of dextrose in urine as modified by the author was applied to the estimation of lactose in milk. The results were trustworthy. CHEMICAL ABSTRACTS.

**[Estimation of Invert-sugar by Fehling's Solution.]** J. D] VAN LEEUWEN (*Chem. Weekblad*, 1919, **16**, 1425—1426).—In the titration of invert sugar solution with Fehling's solution, dilution of the latter with four times its volume of magnesium sulphate solution (0.5 gram per litre) causes the precipitated cuprous oxide to settle rapidly, and thus gives a clear solution for testing with potassium ferrocyanide and acetic acid; the solution must be cooled for this test. W. J. W.

**Estimation of Carbamide by means of Sodium Hypobromite.** E. DEKEUWER and L. LESCOEUR (*Compt. rend. Soc. Biol.*, 1919, **82**, 445—447; from *Chem. Zentr.*, 1919, iv, 350).—In the estimation of pure carbamide by bromine and alkali hydroxide, a slight deficit is always observed which has about the same magnitude when calculated from the nitrogen evolved or from the bromine used; the error is doubled when the calculation is based on the

amount of carbon dioxide formed. The course of the reaction appears to depend on the relative quantities of alkali and carbamide. A factor can be applied based on the results obtained. In the estimation of carbamide in urine, high results are obtained when the calculation is based on the bromine which is utilised (particularly in the case of urines containing sugar), since bromine is also used in the oxidation of substances other than carbamide. The results deduced from the amounts of nitrogen and carbon dioxide formed respectively generally agree well among themselves; in the case of urines containing sugar, the values calculated from carbon dioxide are lower than those reckoned from nitrogen.

H. W.

**Estimation of Carbamide in Blood and Urine.** C. BRAHM (*Deut. med. Woch.*, 1919, **45**, 803; from *Chem. Zentr.*, 1919, iv, 442).—A criticism of Citron's method of estimating carbamide. The latter is not quantitatively decomposed by sodium hypobromite according to the scheme:  $\text{CO}(\text{NH}_2)_2 + 3\text{NaBrO} = 13\text{NaBr} + \text{CO}_2 + 2\text{H}_2\text{O} + \text{N}_2$ , since a proportion of the nitrogen is retained as nitric acid or cyanuric acid. In the author's opinion all methods which are based on the reaction between carbamide and sodium hypobromite are to be rejected. The form of apparatus proposed is also open to many objections.

H. W.

**Estimation of Carbamide in Urine by means of Urease.** ARNOLD HAHN (*Deut. med. Woch.*, 1919, **45**, 911—912); from *Chem. Zentr.*, 1919, iv, 562—563).—The author's method has been modified by Horváth and Kadletz by the introduction of a receiver containing acid; the alteration is regarded as adding an unnecessary complication to the process.

H. W.

**Detection of Hydrocyanic Acid in a Case of Poisoning. Its Post-mortem Transformation into Sulphocyanic Acid.** L. CHELLE (*Compt. rend.*, 1919, **169**, 852—854. Compare A., 1919, ii, 529, 530).—A dog was poisoned by administering potassium cyanide and an autopsy immediately performed, the various organs being divided up and kept in stoppered sterile flasks for various lengths of time. Using the methods previously described (*loc. cit.*), hydrocyanic acid as such, but no thiocyanic acid, was detected after two hours in the brain, lungs, and blood, but not in the liver. After eight days no hydrocyanic acid as such could be detected in any of the organs or the blood, but thiocyanic acid was found in the blood, lungs, and brain, but not in the liver. Further, the amount of thiocyanic acid found in the lungs and brain, but not in the blood, corresponded with far more than the amount of hydrocyanic acid found at the end of two hours. This is explained on the grounds that a certain amount of hydrocyanic acid becomes enclosed in the cells in the first few hours after death and is not set free by the methods of estimation used, but after eight days, as a result of

putrefaction and consequent cytolysis, it is all liberated by the reagents and thus estimated. W. G.

**Estimation of Ferricyanide and Ferrocyanide.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 1618—1626).—The author has investigated the iodometric estimation of potassium ferricyanide. The acidity of the solution has an appreciable influence on the reaction; if the concentration is sufficiently high, accurate results are obtained after allowing the solutions to remain for only half a minute. Rupp's method for the estimation of ferrocyanide is inaccurate. An outline is given of the theoretical interpretation of the iodometric estimation of ferri- and ferro-cyanide. The reducing action of ferrocyanide is increased by rise of temperature.

W. J. W.

**Proteinogenous Amines. II. A Micro-chemical Colorimetric Method for Estimating Iminazole Derivatives.**

KARL K. KOESSLER and MILTON T. HANKE (*J. Biol. Chem.*, 1919, **39**, 497—519).—The method depends on the colour reaction between compounds containing the iminazole ring and sodium *p*-diazobenzenesulphonate. It can be applied directly to practically any iminazole derivative, gives equally good results whether applied to pure solutions or mixtures, and is capable of estimating with a fair degree of accuracy as little as 0.00001 gram of any of the iminazoles. The iminazole derivative is added under certain conditions to a mixture of sodium carbonate and the *p*-diazobenzenesulphonic acid in one cup of a Duboscq colorimeter, and the height of liquid in this cup is set at 20 mm. The other cup is filled with an appropriate indicator solution, and the height varied until the colours match. From tables which have been prepared, the amount of the iminazole derivative can be read off. Certain substances interfere with the method, notably ketones, alcohols, ammonium salts, and proteins. Animal charcoal must not be used to decolorise solutions which it is desired to test for iminazole derivatives, as loss by adsorption occurs. J. C. D.

**Proteinogenous Amines. III. A Quantitative Method for Separating Histamine from Histidine.**

KARL K. KOESSLER and MILTON T. HANKE (*J. Biol. Chem.*, 1919, **39**, 521—538).—The colorimetric process described in the preceding abstract may be utilised for estimating certain components of mixtures of iminazole derivatives. A mixture of these derivatives, such, for example, as that which is formed by the action of bacteria on histidine in the presence of salts and dextrose, is treated with sufficient sodium hydroxide to make the whole a 20% solution of alkali. This solution is extracted repeatedly with amyl alcohol, whereby the histamine, ammonia, methyliminazole, and other amines are removed. This extract is termed the histamine fraction, whilst the residual liquid containing histidine, iminazole, propionic, acetic and lactic acids is called the histidine fraction. The amount of histidine can be determined by an estimation of the

amino-nitrogen in the second fraction. A colorimetric estimation on the same fraction will indicate whether there are other iminazole derivatives present other than histidine.

The histamine and methyliminazole are extracted from the amyl alcohol by 1.0*N*-sulphuric acid, and a colorimetric estimation will give on this extract an indication of the total iminazole substances present. The methyliminazole may be estimated directly by the fact that it is volatile in steam. The colorimetric estimations on these two fractions will give by difference the amount of histamine present.

J. C. D.

**Direct Estimation of Non-amino-nitrogen in the Products of Protein Hydrolysis.** ALMA HILLER and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1919, **39**, 479—488).—An extension of the method of protein analysis introduced by Van Slyke (*A.*, 1915, ii, 851). The filtrate from the phosphotungstates of the diamino-acids, representing 2 or 3 grams of protein, is concentrated to 150 c.c. Portions of this solution are used for estimations of the total nitrogen and amino-nitrogen, as described in the original paper. Of the residue, 100 c.c. are measured into a separating funnel of 500 c.c. capacity, and are rendered free from phosphotungstic acid by extraction with amyl alcohol-ether mixture in the presence of hydrochloric acid. The solution is concentrated in a vacuum to about 50 c.c., and washed into a 100 c.c. volumetric flask. Of this solution, 20 c.c. portions are used for the non-amino-nitrogen estimation. Each portion is placed in a small Kjeldahl flask with 1.2 c.c. of 30% sodium nitrite and 5 c.c. of concentrated hydrochloric acid. When deamination is completed, the solution is neutralised to alizarin with 10% sodium hydroxide and reduced with zinc-copper couple. After making alkaline with magnesium oxide, the ammonia formed by the reduction is removed by boiling, and residual nitrogen is estimated by the Kjeldahl process. The results by this direct method agreed closely, in analyses of caseinogen and gelatin, with the results obtained indirectly by the original procedure.

J. C. D.

**Apparatus for Rapid Gastric Analysis, together with a Method for the Preservation of Starch Solution.** RAYMOND J. MILLER (*J. Ind. Eng. Chem.*, 1919, **11**, 963—964).—A convenient arrangement of burettes, indicator reservoirs and delivery tubes, an automatic pipette, etc., attached to one stand, and intended for the estimation of total acidity, free acidity, and amino-acid nitrogen (formaldehyde method) in gastric fluids. The starch solution is preserved under a layer of liquid "petrolatum," with or without the addition of a small quantity of toluene.

W. P. S.

## General and Physical Chemistry.

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**The Constitution of the Atom and the Properties of Band Spectra.** H. DESLANDRES (*Compt. rend.*, 1919, 169, 1365—1371. Compare A., 1919, ii, 206, 310, 441, 486).—Further evidence is given in support of the views previously published (*loc. cit.*). The author emphasises the fact that the formula given (A., 1919, ii, 206, 310) is only a first approximation, and offers some explanation of the divergencies found in certain cases. W. G.

**Intensity Relations in the Spectrum of Helium.** T. R. MERTON and J. W. NICHOLSON (*Phil. Trans.*, 1919, A, 220, 137—173).—The spectrum of helium has been examined by photographing the radiation in front of an aluminium cathode in a tube containing helium of such a pressure that the thickness of the dark space was about 1 mm. A number of experiments were made with mixtures of helium and other gases, particularly hydrogen. The most striking phenomenon observed relates to the difference in behaviour between the series of helium and parhelium, for, in the former, lines belonging to a series maintain a practically constant intensity ratio at every point, whilst in the latter the relative intensity of any two lines of the same series varies with the distance from the cathode. In the case of lines belonging to the principal series, the seat of maximum emission is closer to the cathode, and falls away with increasing distance from this point more rapidly than in the case of lines belonging to associated series. The diffuse series appear to preserve the most uniform intensity over a wide range of conditions. J. F. S.

**Spectrum of Neon.** F. PASCHEN (*Ann. Physik*, 1919, [iv], 60, 405—453).—An account is given of a very complete examination of the spectrum of neon from  $\lambda$  9840·42 to  $\lambda$  2550·55. A long table is given of the wave-lengths, intensities, and the spectrum combination of each line. The regularities between the lines of the principal and subsidiary series are investigated and discussed. J. F. S.

**Emission Spectra and the Chemical Reactions taking place in the Source of Radiation.** ANGEL DEL CAMPO (*Anal. Fis. Quim.*, 1919, 17, 247—270).—Attention is directed to slight variations in the spectrum of the same element as described by different observers. The author regards these as being due to chemical reactions, notably oxidation and reduction, occurring within the radiant arc. These reactions may be localised, according to circumstances, in the immediate neighbourhood of the electrodes or in the middle of the arc itself, thus giving rise to a "polar effect" in the photograph. This is illustrated in the case of the

silica spectrum, which shows variations as different sections of the arc between the carbon electrodes are examined. The view is expressed that the variations are due to the presence or absence of a reduction product, the suboxide  $\text{SiO}$ . A similar phenomenon is observed with magnesium, and is attributed to the suboxide  $\text{Mg}_2\text{O}$ . In studying the spectra of various specimens of aragonite, three new lines, 2554.6, 2563.8, and 2565.0 Å.U., were observed. These were given by all samples of naturally occurring calcium carbonate examined, but not by pure hydroxide. In both cases the oxide formed is reduced to metal in contact with the carbon. This is immediately re-oxidised in the arc, but in the former case the protective action of the carbon dioxide liberated at the same time ensures the persistence of the metallic vapour for a longer time and range, so that the radiation from the metal is rendered perceptible. Further experiments confirmed the view that the lines in question belong to the calcium spectrum, and are not due to impurities in the substances examined.

W. S. M.

**The Emission of Positive Luminous Particles at High Temperatures by the Alkali Metals.** G. A. HEMSALECH (*Compt. rend.*, 1920, 170, 44—47).—Using the graphite plate with a layer of carborundum, the plate being electrically heated as previously described (compare this vol., ii, 1, 2), it is shown that if the plate is first covered with a thin layer of the chloride, carbonate, or oxide of one of the alkali metals, and this, in turn, covered with carborundum, positively electrified particles are emitted at varying temperatures. All the elements in the alkali group emit positive particles, and for a given temperature the extension and development of the luminous trajectories vary directly with the atomic weights, and in consequence the critical temperature, or temperature at which the phenomenon is apparent, varies inversely with the atomic weight. For lithium the critical temperature is  $2700^\circ$ , and for caesium  $1900^\circ$ . Two hypotheses are put forward to explain this phenomenon, but further work is necessary before a definite explanation can be given.

W. G.

**[The Emission of Positive Luminous Particles at High Temperatures by the Alkali Metals.]** A. DE GRAMONT (*Compt. rend.*, 1920, 170, 47).—The author states that Hemsalech used a monochromatic, optical pyrometer for the temperature measurements in his work (preceding abstract). The instrument was calibrated and corrected up to  $2500^\circ$ , above which temperature extrapolation was necessary. At  $2700^\circ$  the temperature readings are accurate to  $\pm 50^\circ$ .

W. G.

**The Direct Arc Spectra of Metals with Moderately High Melting Points.** A. DE GRAMONT (*Compt. rend.*, 1920, 170, 31—38).—A comparison of the direct arc spectra with the spark spectra and the carbon arc spectra in the case of the metals zinc, cadmium, tin, lead, antimony, bismuth, magnesium, and aluminium. By the photographic device employed, the three spectra were obtained in

successive coincidence, thus permitting of a direct comparison of the rays. By this means, it has been possible to detect in the direct ray spectra on the one hand certain rays of the spark spectra, considered by Lockyer as strengthened, and which occur in the direct spectra with a marked intensity, and on the other certain rays of the spark spectra, also classed as strengthened, but which are only fugitive in the direct arc spectra. The latter group of rays appears at the positive pole at the moment of striking the arc. They can most easily be seen by alternately making and breaking the arc. The detailed results are given for each of the metals, and the general conclusions to be drawn are that the arc spectra must not be considered as invariable and always identical. They are subject to considerable variations, not only in the intensities of certain rays, but also in the appearance of the rays, these variations being closely connected with the intensity of the current producing the arc.

W. G.

**New Lines in the Arc Spectrum of Silver between  $\lambda$  4500 and  $\lambda$  2300.** M. A. CATALÁN (*Anal. Fis. Quim.*, 1917, 15, 483—486).—Measurements of eighty new lines were made with wave-lengths corresponding with similar lines in the spark spectrum described by Exner and Haschek ("Tabellen der Funkenlinien," 1902).

W. S. M.

**New Lines in the Arc Spectrum in Air of Iron between 2300 and 1980 Å.U.** S. PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1917, 15, 434—444).—Measurements of more than 288 new lines in the arc spectrum of iron are given, extending the spectrum from 2300 Å.U. to 1994 Å.U.

W. S. M.

**New Lines in the Arc Spectra of Nickel and Cobalt between 2300 and 2000 Å.U.** S. PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1918, 16, 338—350).—A total of 66 new lines for nickel and 165 for cobalt in the given range was measured.

W. S. M.

**Photochemistry of Thallous Chloride.** CARL RENZ (*Helv. Chim. Acta*, 1919, 2, 704—717).—The action of light on thallous chloride has been investigated; the action was carried out with the dry substance and with thallous chloride under water, hydrochloric acid, ammonia, ethylamine, ethyl alcohol, glycerol, toluene, xylene, and pyridine. In all cases, a darkening occurs, which passes through the shades greyish-brown, dark greyish-brown, and blackish-brown. The change is due to the formation of a photo-thallous chloride and thallous-thallic chloride. Hydrochloric acid, even in traces, retards the formation of the photo-chloride, and, after prolonged illumination, various yellow, double thallous-thallic chlorides are formed. Nitric acid and sulphuric acid have a similar retarding action on the formation of the photo-chloride. Ammonia, ethylamine, and the above-named organic substances act as sensitizers in the reaction, and many inorganic salts have a photo

catalytic action. The sensitiveness of thalious chloride to light depends on its method of formation. Thalious chloride precipitated by metal chlorides is more sensitive than that precipitated with hydrochloric acid, even though the acid has been thoroughly washed out.

J. F. S.

**Diffusion of Radium Emanation in Water.** EVA RAMSTEDT (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 5, 1—14).—The velocity of diffusion of radium emanation in water at 14° has been determined by means of an apparatus containing a number of metal plates immersed in water. The coefficient of diffusion is found to be 0.820 cm. per day, a value which is of the same dimensions (0.985 at 18°) as that recently found by Rona (A., 1917, ii, 286). Calculating from this value, the product  $D\sqrt{m}$  is found to be 12.2, and the molecular diameter of radium emanation  $1.85 \times 10^{-8}$  cm.

J. F. S.

**Ionisation Potential of Helium.** J. FRANCK and P. KNIPPING (*Physikal. Zeitsch.*, 1919, **20**, 481—488).—Using as source of electrons a glowing wire in helium of pressure 1.5 mm., the resonance potential is found to have the value  $20.5 \pm 0.25$  volts, and from this value the ionisation potential is calculated to  $25.3 \pm 0.25$  volts. Experimentally, the ionisation potential of helium is found to be  $25.4 \pm 0.25$  volts, and the resonance potential has the same value as before. The potential necessary for the removal of both electrons from the helium atom is also determined, and the value  $79.5 \pm 0.3$  volts obtained. The present results are in agreement with those of Horton and Davies (A., 1919, ii, 210), and indicate that the helium atom is much less stable than is indicated by the atomic model of Bohr and Landé.

J. F. S.

**Conductivity. VI. Behaviour of Mixtures of Two Salts containing a Common Ion in Anhydrous Formic Acid Solution.** H. I. SCHLESINGER and F. H. REED (*J. Amer. Chem. Soc.*, 1919, **41**, 1921—1934. Compare A., 1919, ii, 91).—The conductivity of potassium formate in anhydrous formic acid solution has been determined at 25° over the range 0.1207N—0.3266N. The degree of ionisation and the ionisation constant are calculated in each case, and the latter constant has the value 1.090. Similar measurements were also made for sodium formate and lithium formate; these salts have ionisation constants 0.810 and 0.557 respectively. Conductivity measurements were also made for mixed solutions of sodium and potassium formates, lithium and potassium formates, strontium and potassium formates, and strontium and calcium formates, all in anhydrous formic acid and at 25°. A method of calculating from the ionisation constants the degree of ionisation of each of two salts containing a common ion, when the two salts are both present in solution, has been developed for the case in which both salts obey the law of mass action. It is found that in mixtures of sodium and potassium formates, as



well as of lithium and potassium formates, the mass law is obeyed by both of the highly ionised salts present. On the other hand, solutions of mixtures containing, as one or as both of the salts, alkaline earth formates do not conform to the law, although these uni-bivalent salts when in solution alone seem to follow the law over a certain range of concentration. This appears to make it quite certain that whenever the agreement of the salt with the law is an accidental one, solutions of mixtures containing such a salt will not obey the law. Hence it may be definitely concluded that the agreement between the behaviour of the alkali metal formates, in anhydrous formic acid solution, and the demands of the mass law is a real and not an accidental one. When the total concentration of mixed solutions becomes relatively great, deviation from the mass law occurs also in the solutions which contain uni-univalent formates. It has been found that this deviation begins when the concentration of the non-ionised molecules of one of the salts reaches the same value as that at which deviation begins in the solution of that salt by itself. This seems to be independent of the concentration of the other molecular species present, and to indicate that in concentrated solutions it is the non-ionised molecules, and not the ions, which cause deviation from the mass law, or at least the non-ionised molecules cause deviation at lower concentrations than do the ions.

J. F. S.

**Conductivity. VII. Transference Numbers of the Formates of Sodium, Potassium, and Calcium in Anhydrous Formic Acid.** H. I. SCHLESINGER and E. N. BUNTING (*J. Amer. Chem. Soc.*, 1919, **41**, 1934—1945. Compare preceding abstract).—The transport numbers of solutions of sodium, potassium, and calcium formate in anhydrous formic acid have been determined by the usual method at 25° for a number of concentrations between 0.09*N* and 0.4*N*. The ionic conductivity of the formate ion is calculated to be 51.5, that of sodium ion 14.6, and potassium 17.5. The transport number of the potassium ion changes with concentration. This is tentatively explained on the assumption that the ion is solvated, and a method for calculating the extent of solvation from the transport numbers is suggested. The results indicate that, if the assumptions made in the calculation are correct, each potassium ion is combined with from six to eight molecules of formic acid. The transport numbers obtained for calcium formate do not substantiate the view that calcium formate in formic acid solution ionises either entirely as a uni-univalent salt or entirely as a uni-bivalent salt. It is therefore possible that both methods of ionisation occur.

J. F. S.

**Electric Conductivity of Weakly Ionised Neutral Salts.** OLOF SVANBERG (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 26, 1—7).—The equivalent conductivity of potassium antimonyl tartrate and cupric acetate has been determined over the range *N*/4 to *N*/1024 at temperatures 0—65°. In the case of potassium antimonyl tartrate the equivalent conductivity increases from 64.4 at

$d=4$  to 134.5 at  $d=1024$  at  $25^\circ$ ; the more concentrated solutions (up to  $N/32$ ) at all temperatures follow the Ostwald dilution law, but beyond this point the conductivity increases more rapidly than is demanded by any of the formulæ for the extrapolation of the infinity value. There is no evidence that potassium antimonyl tartrate ionises as the potassium salt of antimonyl tartaric acid, and it is also shown that the salt is not greatly hydrolysed in any of the solutions examined. In the case of cupric acetate the equivalent conductivity at  $25^\circ$  increases from 10.8 in  $N$ -solutions to 75.3 in  $N/1024$  solutions, which indicates considerable hydrolysis. The equivalent conductivity at infinite dilution has been obtained by extrapolation, and the following values found: potassium antimonyl tartrate,  $0^\circ$ ,  $\Delta_\infty = 76$ ;  $25^\circ$ ,  $\Delta_\infty = 154$ ;  $50^\circ$ ,  $\Delta_\infty = 260$ ;  $65^\circ$ ,  $\Delta_\infty = 308$ , copper acetate,  $25^\circ$ ,  $\Delta_\infty = 90$ .  
J. F. S.

**Relation between the Electrical Phenomenon in Cloud-like, Condensed, Odorous Water Vapours and Smell-intensity.** H. ZWAARDEMAKER and H. ZEEHUISEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 175—178).—Odorous organic substances in dilute aqueous solution when sprayed yield electric charges. It is found on diluting these solutions to such an extent that the electrical phenomena are only just appreciable that the odour is also just appreciable. It is suggested that both these properties depend in a complicated way on (a) the volatility of the substances, and (b) the lowering of the surface tension of the solvent (compare A., 1918, ii, 351).  
J. F. S.

**Dielectric Constants considered in Connexion with the Theory of Dipolar Molecules.** OSKAR KLEIN (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 24, 1—48).—The dielectric constants have been determined for a number of solutions in organic liquids by means of a resonance method. The solutions examined consisted of (1) methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, amyl alcohol, allyl alcohol, benzyl alcohol, acetone and methyl ethyl ketone in benzene; (2) ethyl alcohol, butyl alcohol, and benzyl alcohol in chloroform. It is shown that the resonance method, which is the method used technically for measuring capacity, is well suited to the measurement of dielectric constants. Solutions of the alcohols in benzene or chloroform of the same normality have the same dielectric constant. Thus  $N$ -solutions of alcohols in benzene have a dielectric constant 2.63, in chloroform solution 5.68. Acetone and methyl ethyl ketone have the same value in benzene solution, namely, 3.09. J. J. Thomson's rule that related substances have the same value for  $(\epsilon-1)M$  holds absolutely for mixtures of the alcohols and water. Some measurements of Pohrt on the dielectric constants of gases are examined, and yield the temperature-coefficient which is demanded by the dipolar theory. The formula of Debye  $(\epsilon-1)/(\epsilon+2) \cdot v = A/T + B$  is changed to the form  $(\epsilon-1)(v-b) = A/T$ , in which for substances which belong to a single group the relationship  $AM = L$  obtains;  $L$  is a constant pro-

portional to the square of the molecular moment, and  $M$  is the molecular weight. These formulæ combine the above-named rules and are in keeping with the dipolar theory. The constant  $L$  has been calculated from several of the experiments, and the values for alcohol (67,000) and acetone (180,000) obtained. The formula  $(\epsilon - 1) = A/T(v - b)$  is applied to the dependence of the dielectric constant on temperature in the case of water, and found to be in keeping with facts. The formula  $K = L/T = M(v - b)(\epsilon_0 - 1) + \mu/[1 + k(\epsilon_0 - 1)]$  holds for infinitely dilute solutions, and together with  $(\epsilon - 1) = A/(v - b)T$  furnishes an exact method for calculating the constants  $K$  and  $b$ . The approximate formula  $K = \mu/[1 + k(\epsilon_0 - 1)]$  is deduced from the above, and allows the determination of  $K$  from a knowledge of the dielectric constant of solutions of the substances concerned.

J. F. S.

**Dielectric Constants of Typical Aliphatic and Aromatic Hydrocarbons, *cyclo*Hexane, *cyclo*Hexanone, and *cyclo*Hexanol.** THEODORE W. RICHARDS and J. W. SHIPLEY (*J. Amer. Chem. Soc.*, 1919, **41**, 2002—2012).—The dielectric constants of a number of hydrocarbons have been determined at 20°, except in the case of *cyclo*hexanol, which was determined at 25°, by a modified Nernst type of apparatus. The percentage error of the method was much decreased by the use of larger suitably balanced condenser troughs. The following values have been obtained as the mean of several concordant measurements: hexane, 1.876; heptane, 1.973; octane, 1.962; *n*-nonane, 1.967;  $\delta$ -methyloctane, 1.967;  $\beta$ -methyl-octane, 1.967;  $\beta\zeta$ -dimethylheptane, 1.987;  $\beta\delta$ -dimethylheptane, 1.89;  $\beta\epsilon$ -dimethylheptane, 1.89; decane, 1.956; xylene (commercial), 2.375; *m*-xylene, 2.377; ethylbenzene, 2.482; *n*-propylbenzene, 2.364; cumene, 2.400; mesitylene, 2.356; *tert*-butylbenzene, 2.384; *cyclo*hexane, 2.055; *cyclo*hexanone, 18.2; and *cyclo*hexanol, 15.0. The present results are in moderate agreement with the values of previous observers, although in many cases no previous measurement is on record.

J. F. S.

**Relation between the Specific Inductive Capacity of an Electrolyte and the Electric Potential of a Metal placed in it.** D. L. ULREY (*Physical Rev.*, 1919, **12**, 47—58).—Attention is called to the inadequacy of the Nernst theory of the mechanism of galvanic current production. This theory omits an essential factor, namely, specific inductive capacity of the electrolyte, and employs two hypothetical quantities, metal solution pressure and osmotic pressure of the ions. Transfer of ions between metal and electrolyte is probably brought about by electrical forces, the magnitude of which depends on the specific inductive capacity of the medium. The potential difference between electrodes of the same kind in a two-solution cell was measured for several different percentage mixtures of two liquids for four different cases, and in each case was shown to be strictly proportional to the difference in the specific inductive capacity of the two solutions. The following systems were measured: (a) ethyl alcohol-water (solution of cupric

chloride), with copper electrodes (electrode in the aqueous solution electronegative); (b) ethyl alcohol-water, with calomel electrodes (electrode in the water electropositive); (c) acetone-water, with calomel electrodes (electrode in the water electropositive); (d) methyl alcohol-water, with calomel electrodes (electrode in the water electropositive); and (e) solution of carbamide-water, with platinum electrodes (electrode in the water electropositive). In two cases investigated with copper electrodes, one with platinum electrodes, and six with calomel electrodes, the direction of the *E.M.F.* of the cell is in accordance with the theory that the loss of ions from an electrode is dependent on the specific inductive capacity of the electrolyte rather than on the concentration of those ions in the electrolyte and a solution tension of the electrode. Results obtained further substantiate the theory that the more electropositive metals have the higher specific inductive capacities. CHEMICAL ABSTRACTS.

**Changes of Potential in an Oxidising Agent by Ultra-violet Light.** TORSTEN SWENSSON (*Arkiv. Kem. Min. Geol.*, 1917, 6, No. 12, 1—32).—The effect of ultra-violet light on the potential of solutions of potassium dichromate in sulphuric acid has been examined. The source of light employed was a quartz mercury lamp, and the solutions were maintained at 18° during illumination. The platinum electrode used in the measurements was bright, since it was found that the same value was obtained with both bright and platinised electrodes, but the former reached equilibrium more rapidly. It is shown that during the illumination with ultra-violet light of a solution of potassium dichromate and sulphuric acid, and also during the illumination of either sulphuric acid, potassium dichromate, or chromic acid alone, a change in potential occurs. To achieve this result it is not necessary to illuminate the platinum electrode. In the case of dichromate and sulphuric acid a speedy increase in the potential occurs; whilst when sulphuric acid and dichromate are illuminated separately a decrease in potential occurs. The potential is also decreased for pure chromic acid, and consequently it is shown that the positive effect does not depend on the liberation of this acid on the addition of sulphuric acid to the dichromate. The speedy change in *E.M.F.* is caused by the ultra-violet rays, and is not observed when the action takes place in glass vessels. Both the increase and decrease of *E.M.F.* are of a photochemical nature. Over the range examined the potential change is independent of dilution. The change of potential is in a high degree dependent on the composition of the solution, and shows a maximum at about 75 mol. % potassium dichromate. The decrease in *E.M.F.* after the interruption of the illumination takes place gradually. It is also dependent on the composition, and is most rapid for pure sulphuric acid. It is further greatly dependent on the temperature, and after a moment's boiling the potential becomes normal again. Solutions which have been illuminated, but have returned to their original potential, show on renewed illumination changes in the velocity of the potential

increase and the maximum value. On very bright illumination a rapid increase in *E.M.F.* was observed, which, on interruption of the light, sank very quickly. In this case the illumination of the electrode is essential.

J. F. S.

**Polarisation Tensions of Iron in Solutions of its Complex Salts. Relations between these Tensions and the Dissimulation of Analytical Characters of Ferric Ions.** N. R.

DHAR and G. URBAIN (*Compt. rend.*, 1919, **169**, 1395—1397).—The electrolytic cell consists of two half elements joined by a solution of potassium chloride. One half element consists of a metallic electrode in a solution of one of its salts, and the other is an electrode of mercury in a solution of calomel and potassium chloride. The polarisation tension is defined as the difference between the *E.M.F.* of the whole cell and the corresponding value as found in Auerbach's results (compare A., 1912, ii, 123) for the half element containing the mercury electrode. This tension should depend on the number of free metallic ions in the solution, the tension diminishing as the number of ions increases. These measurements should, therefore, in the case of complex salts, give an indication as to how far the metallic constituent of the complex ion is dissimulated. The results obtained with simple and complex iron salts are in agreement with those obtained by Pascal (A., 1909, ii, 487) as to their molecular magnetic susceptibilities.

W. G.

**Hydrogen Overvoltage. II. Applications of its Variation with Pressure to Reduction, Metal Solution, and Deposition.**

D. A. MACINNES and A. W. CONTIERI (*J. Amer. Chem. Soc.*, 1919, **41**, 2013—2019. Compare A., 1919, ii, 131).—The increase of hydrogen over-voltage with diminished pressure is shown to follow, in a nearly quantitative manner, from the theory of MacInnes and Adler (*loc. cit.*). The effect of a change in the gaseous pressure on several chemical processes involving the evolution of hydrogen has been studied. The changes in rates of reaction and in reaction efficiencies were found in each case to be in the directions which follow from the change of hydrogen over-voltage with pressure; that is, a decrease of gaseous pressure produces (a) a decrease in the rate of solution of metals in electrolytes, (b) an increase in the efficiency of reductions by metals, and (c) an increased efficiency of metal deposition. The theory explaining the fluctuation of over-voltage accompanying the evolution of a single bubble of hydrogen from a platinum electrode is discussed.

J. F. S.

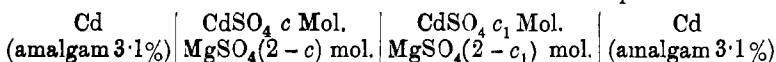
**Determination of the Hydrogen Exponent.** J. PINKHOF (*Chem. Weekblad*, 1919, **16**, 1168—1172).—If, in Poggendorff's method, the normal electrode is replaced by an electrode which does not differ in potential from that of the hydrogen electrode, then, if the composition of the liquid is known and its relation to the potential, the potential of the hydrogen electrode, and therefore the hydrogen exponent, can be determined. The results obtained with a silver electrode in a solution of silver cyanide in

excess of potassium cyanide were not accurate. An electrode of cadmium amalgam in solutions of cadmium salt of various concentrations was found to be suitable. A simple apparatus for the determination is described.

W. J. W.

### Applicability of the Gas Laws to the Strong Electrolytes.

J. N. BRÖNSTED (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, 5, No. 25, 1—19).—A number of solubility and *E.M.F.* measurements have been carried out with the object of testing the hypothesis. "The gas laws hold for ions or salts when other salt solutions are employed as solvents, the concentration of the latter being large when compared with the concentration of the dissolved salt." The *E.M.F.* of cadmium|cadmium sulphate in magnesium sulphate solution has been measured. The element is made up:



The value of  $c$  and  $c_1$  varied between 0.1*M* and 1/640*M*, and the temperature was 20° and 39.4°. The potentials obtained are compared with those demanded by the gas laws, and an excellent agreement found. The solubility of dinitrotetra-aminocobalt nitrate, both  $\alpha$  and  $\beta$  varieties, has been determined at 0° and 20° in water, and in solutions of various concentrations of potassium formate, thiocyanate, hydroxide, and nitrate, nitric acid, sodium oxalate, and sodium nitrate. The values obtained are in keeping with the demands of the gas laws.

J. F. S.

**The Electroaffinity of Aluminium. I. The Ionisation and Hydrolysis of Aluminium Chloride. II. The Aluminium Electrode.** JAROSLAV HEYROVSKÝ (*T.*, 1920, 117, 11—26, 27—36).

### Occlusion of Hydrogen and Oxygen by Metal Electrodes.

EDGAR NEWBERY (*J. Amer. Chem. Soc.*, 1919, 41, 1887—1892, 1895—1898); EARLE A. HARDING and DONALD P. SMITH (*ibid.*, 1892—1894, 1897—1898).—Polemical. In the first paper Newbery gives a theoretical discussion of the paper put forward by Harding and Smith (*A.*, 1918, ii, 424), and a criticism of the theory put forward as to the condition of the occluded hydrogen in palladium. The following papers contain replies and counter-replies by Harding and Smith, and Newbery.

J. F. S.

### Electro- and Thermo-chemical Investigation of the Cells Cu or Cu Amalgam | CuSO<sub>4</sub>-Hg<sub>2</sub>SO<sub>4</sub> | Hg.

L. W. ÖHOLM (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, 5, No. 4, 1—20).—The *E.M.F.* of the elements Cu|N-CuSO<sub>4</sub>, Hg<sub>2</sub>SO<sub>4</sub>(sat.)|Hg and Cu(12% amalgam)|N-CuSO<sub>4</sub>, Hg<sub>2</sub>SO<sub>4</sub>(sat.)|Hg have been measured at 10°, 15°, 17°, 20°, 25°, and 30° daily for a period of two months. The copper amalgam cells are fairly constant and easily reproducible, and the variation of the *E.M.F.* with temperature is represented by the formula

$$E_t = 0.35030 - 0.00064(t - 20) - 0.0000025(t - 20)^2.$$

The cells with a copper electrode had a slightly higher (0.004—0.005

volt) *E.M.F.* than the amalgam cells, and it is nothing like so constant.  $E_{20}=0.3542$  and  $dE/dT=-0.00072$  volt. The chemical energy of the copper cell is calculated, and the value  $Q=24,860$  cal. obtained. The quantity  $Q$  is regarded as made up of three quantities,  $q_1$ ,  $q_2$ , and  $q_3$ ,  $q_1$  being the heat change when 1 gram-atom of copper is withdrawn from the amalgam,  $q_2$  the difference in the heat of formation of copper and mercury sulphate, and  $q_3$  the heat change accompanying the withdrawal of water from the solution by the newly formed copper sulphate. These three values are calculated to  $q_1=-1297$  Cal. at  $20^\circ$ ,  $q_2=7600$  Cal., and  $q_3=18.527$  J. F. S.

**Passivity of Cobalt.** HORACE G. BYERS and CURTIS W. KING (*J. Amer. Chem. Soc.*, 1919, **41**, 1902—1908).—When cobalt is used as anode in the electrolysis of  $0.02N$ -sulphuric acid or sodium sulphate at  $0^\circ$ , it becomes passive if a high current density is employed, but with low current density it remains active; if potassium dichromate is present, it readily assumes the passive condition in all circumstances. The passive state is indicated by an increased drop in potential, a decreased current, by the evolution of oxygen, and by the failure of the cobalt to pass into solution. The potential measurements of a cobalt-platinum cell with various electrolytes, and a comparison with similar results with iron and nickel, show that when the cobalt becomes passive there is a marked increase in voltage across the cell. The potential measurements show that this is due to a change in the potential of cobalt as it changes from the active to the passive condition. Cobalt may therefore be classified with the passive metals, since it exhibits all the characteristics of iron and nickel when they are passive. The essential difference between cobalt and the other passive metals lies in the fact that cobalt, when used as an anode, will not become passive at the low current densities required by nickel and iron. If cobalt has once assumed the passive condition, it will remain so, even though the current density is reduced. In the absence of the anodic relation, cobalt becomes active in acid solution more readily than nickel. J. F. S.

**Activity Coefficient for Ions.** NIELS BJERRUM (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 16, 1—21).—A theoretical paper in which activity coefficients are considered with the object of bringing strong electrolytes into line with the ionic hypothesis. The *activity coefficient* is defined as the effect of the interionic forces on the activity of the ions, the *conductivity coefficient* as the influence of the interionic forces on the conductivity, and the *osmotic coefficient* as the influence of the interionic forces on the osmotic pressure. Various relationships between these and other similar coefficients are evolved mathematically. J. F. S.

**Comparative Electrolysis of Various Alkali Chlorides.** E. BRINER, (MLLE.) A. TYKOCINER, and B. ALFIMOFF (*Helv. Chim. Acta*, 1919, **2**, 666—672).—Solutions of the chlorides of sodium,

lithium, and potassium of various concentrations have been electrolysed, and the relative current yields of alkali hydroxide compared. After the passage of 50,000 coulombs through 3.1*N*-solutions of these salts, it is shown that the total current yields are respectively for lithium, sodium, and potassium 75%, 82.5%, and 87%. In the case of lithium chloride, two cases are considered: (a) Where the initial concentration of lithium chloride lies on the ascending branch of the conductivity curve (concentrations below 5*N*); here the fraction of the current carried by the lithium chloride diminishes, due to the presence of lithium hydroxide and to the reduction of the salt concentration. (b) Where the initial concentration lies on the descending branch of the conductivity curve (concentrated solutions); here the yield is diminished by the lithium hydroxide present, but it is increased by the fact that the reduction of the lithium chloride concentration brings with it an improvement of the conductivity of the salt.

J. F. S.

### The Transport Number of the Ions of Cadmium Iodide.

GEORGES HEYM (*Ann. Physique*, 1919, [ix], 12, 443—454).—From a series of measurements, it is shown that the transport number of iodine ions varies from 0.55 to 1.0 for solutions of cadmium iodide in which the concentration varies from 0.007 to 0.07 gram of iodine per litre.

W. G.

**Electrochemistry of Uranium and the Single Potentials of Some Oxides of Uranium.** CHESTER A. PIERLÉ (*J. Physical Chem.*, 1919, 23, 517—553).—The electrolysis of uranium compounds in various solvents and under many conditions has been investigated. It is shown that in aqueous solutions with low current density, uranyl salts deposit, in the first place, hydrated uranic oxide,  $\text{UO}_3 \cdot \text{H}_2\text{O}$ , which is changed as the electrolysis proceeds to a black oxide of varying composition. With higher current density, uranyl sulphate is reduced to uranous sulphate, but in the presence of free acid the deposit obtained is small in amount and poorly adherent, although metallic in appearance. In neutral or alkaline solutions, the deposit formed is a mixture of black and yellow oxides. The use of a porous cup diaphragm does not change the character of the deposits. The deposit obtained when alkaline uranyl tartrate or citrate solutions are electrolysed is an oxide much richer in uranium than that deposited from solutions acidified with tartaric or citric acid. The conductivity of non-aqueous solutions of uranyl salts is a function of the water present, and the deposits formed are oxides contaminated with organic matter. Anhydrous pyridine dissolves anhydrous uranium tetrachloride to form conducting solutions; these, on electrolysis, deposit a compound containing uranium and pyridine on the cathode. Solutions of uranium tetrachloride in acetone do not yield metallic uranium on electrolysis; the solution is a good conductor of electricity. The deposit obtained replaces mercury from mercurous sulphate. Uranium tetrachloride reacts with anhydrous acetone, forming  $\beta\beta$ -dichloropropane. During electro-



lysis, hydrogen is evolved. Solutions of potassium uranyl fluoride, whether acid, alkaline, or neutral, form a deposit containing fluorine; in acid solution, the deposit is  $\text{UF}_4 \cdot 6\text{H}_2\text{O}$ ; neutral and alkaline solutions give a deposit containing uranium tetrafluoride and uranium oxide. Deposits obtained from neutral solutions of potassium uranyl cyanide consist of pure potassium uranate. When acidified with hydrocyanic acid, the deposit is the yellow, hydrated oxide contaminated with a little of the black oxide. The single potentials of the metal and the oxides have been measured by pasting the finely powdered material on a platinum electrode with gelatin. The following potentials of the more stable oxides have been obtained:  $\text{U}_3\text{O}_8 | \text{UO}_2(\text{NO}_3)_2$ , 14.3 grams per litre  $\parallel = 0.776$  volt;  $\text{UO}_3 \cdot \text{H}_2\text{O} | \text{UO}_2(\text{NO}_3)_2 \parallel = -0.860$ ; black oxide from aqueous uranyl salts  $| \text{UO}_2(\text{NO}_3)_2 \parallel = -0.6872$  volt; uranium 91.49%  $| \text{UO}_2(\text{NO}_3)_2 \parallel = -0.093$  volt. Uranous oxide,  $\text{UO}_2$ , gives a single potential identical with that obtained for the green oxide,  $\text{U}_3\text{O}_8$ . The black deposit formed when uranium salts are electrolysed is not  $\text{U}_3\text{O}_8 \cdot 2\text{H}_2\text{O}$ , as stated by Smith (*Amer. Chem. J.*, 1879, 1, 329), but a compound,  $\text{U}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ , and it has a different potential to that of  $\text{U}_3\text{O}_8$ .

J. F. S.

**Johan Gadolin's Electrochemical Theory, its Origin and Development.** H. G. SÖDERBAUM (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, 5, No. 9, 1—14).—Historical.

T. S. P.

**Diamagnetic Phenomenon in Luminous Nitrogen and the Magnetic Behaviour of its Band Spectrum.** W. STEUBING (*Physikal. Zeitsch.*, 1919, 20, 512—519).—The intensity changes of the nitrogen bands in a magnetic field have been examined with the magnet in various positions. It is found that if a flat bulb 33 mm. in diameter is blown in the middle of the tube and the tube filled as for an ordinary spectrum observation, the light passes across the bulb in the ordinary way, except that the positive column is slightly broadened. When the field is made active the middle of the bulb is filled with a blue, luminous sheath, which extends up to the walls and is at right angles to the lines of force of the field. This sheath has an identical spectrum with the negative luminescence, and is probably to be accounted for by the diamagnetic molecules setting themselves at right angles to the magnetic lines.

J. F. S.

**Magnetic Properties of some Rare Earth Oxides at Low Temperatures.** E. H. WILLIAMS (*Chem. News*, 1919, 119, 287—288).—The magnetic susceptibility of the oxides of dysprosium, erbium, gadolinium, samarium, neodymium, lanthanum, and yttrium has been determined at a series of temperatures from  $20^\circ$  to  $-140^\circ$ . The following values are given: Dysprosium oxide,  $20^\circ$ ,  $X \times 10^6$ , 233.3°;  $0^\circ$ , 250.0;  $-40^\circ$ , 291.3°;  $-80^\circ$ , 347.4;  $-100^\circ$ , 384.2;  $-120^\circ$ , 430.2;  $-140^\circ$ , 490.0. Erbium oxide,  $20^\circ$ , 188.6;  $0^\circ$ , 201.7;  $-40^\circ$ , 234.8;  $-80^\circ$ , 282.3;  $-100^\circ$ , 314.8;  $-120^\circ$ , 355.0;  $-140^\circ$ , 402.8. Gadolinium oxide,  $20^\circ$ , 129.7;  $0^\circ$ , 138.2;  $-40^\circ$ , 160.7;  $-80^\circ$ , 194.2;  $-100^\circ$ , 217.0;  $-120^\circ$ , 244.6;  $-140^\circ$ , 279.0.

In all cases the oxides were purer than 99.5%. In the case of samarium oxide the susceptibility at  $-140^{\circ}$  was about 10% larger than at  $20^{\circ}$ . Yttrium oxide increases in susceptibility with decrease in temperature, but very slightly, and since the susceptibility is less than  $1 \times 10^{-6}$  the experimental error is relatively large. It is shown that the product of the susceptibility and the absolute temperature is not constant, but decreases with falling temperature to a slight extent.

J. F. S.

**The Paramagnetism of Solid Salts and the Theory of the Magneton.** B. CABRERA (*Anal. Fis. Quim.*, 1918, 16, 436—449).—A mathematical discussion of the Curie-Langevin law when the mutual actions of the paramagnetic atoms are no longer negligible.

W. S. M.

**Furnace Temperature Regulator.** WALTER P. WHITE and LEASON H. ADAMS (*Physical Rev.*, 1919, 14, 44—48).—By making the heating coil of an electric furnace one arm of a Wheatstone bridge, and combining this with a galvanometer regulator, thus keeping the resistance of the coil constant, the temperature of electric furnaces may be kept constant. This device is effective regardless of variations in the current supply, and requires no attention, particularly in the case of furnaces which are not directly influenced by the temperature of the room or where the surrounding air is kept constant. The arrangement operates as follows: Changes in the temperature of the furnace, and consequently in the resistance of the heating coil, operate a boom which either hits or misses a contact-maker which controls a suitable relay. This relay operates a larger magnet, which controls the main current. The power available in this regulator is very large; nothing has to be inserted into the furnace cavity, and the lag is practically non-existent. The regulator is often almost at its best under conditions most unfavourable to other regulators. Using this regulator, the authors have kept a small furnace constant to within  $0.1^{\circ}$  for hours at temperatures from  $500^{\circ}$  to  $1400^{\circ}$ .

J. F. S.

**An Analysis of the Radiation Emitted in Gaseous Explosions.** W. T. DAVID (*Phil. Mag.*, 1920, vi, 39, 84—95).—In explosions of coal-gas and air, and of hydrogen and air, the ratio of the energy in the  $2.8 \mu$  radiation emitted to that in the radiation of longer wave-length decreases as the temperature decreases. In the neighbourhood of  $1200^{\circ}$  abs. the  $2.8 \mu$  radiation decreases very rapidly with the temperature, and is negligible at  $1000^{\circ}$  abs. Radiation of longer wave-length is emitted after the temperature has fallen to  $900^{\circ}$  abs., but at this temperature the emission is small. The ratio of the energies in the  $2.8 \mu$  and the  $4.4 \mu$  radiation in coal-gas and air mixtures appears to depend on the composition of the mixture and the temperature. The loss of heat by radiation expressed as a percentage of the heat of combustion of hydrogen and air mixtures, between the limits of composition of 10 and 25.4% of combustible gas, decreases very rapidly as the latter increases.

The variation for mixtures of coal-gas and air between 9·8 and 15% is small. The author attempts a theoretical explanation of these results on the following lines. The intra-molecular energy acquired on combustion by the freshly-formed molecules of carbon dioxide and water is not equally partitioned over the various internal degrees of freedom of the molecules. When the combustion is gentle the intra-molecular energy is concentrated in the rotational degrees of freedom, and in such very low frequency vibrations as the molecules may be capable of executing. As the combustion becomes more violent the higher frequency vibrations share in this energy, and it is possible that during combustion of extreme violence equipartitioning of energy amongst all the internal degrees of freedom of the molecules may be approached momentarily. This is believed to be capable of explaining many phenomena of explosive combustion, such as the pre-pressure period.

J. R. P.

**Isothermals of Monatomic Substances and their Binary Mixtures. XX. Isothermals of Neon from 20° to -217°.**

C. A. CROMMELIN, J. PALACIOS MARTINEZ, and H. KAMMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 108—118. Compare A., 1917, ii, 407; 1918, ii, 9).—The isothermals of neon have been determined over the range 20° to -217° up to a pressure of 90 atms. by the method previously described. From the results of the experiments the authors have calculated the virial-coefficients from the equation of state. It is shown that the  $pv_A$  values obtained in the present work agree in a very satisfactory manner with the older measurements. Only in the isothermal -217·52° is any marked divergence visible, and here the divergence does not exceed 0·5%, whilst for the isothermal -200·08° they do not reach 0·1%.

J. F. S.

**A New Improvement of the Equation of State of Fluids.**

E. ARIÈS (*Compt. rend.*, 1919, **169**, 1140—1143).—A mathematical discussion of the subject.

W. G.

**Equation of Condition.** FRED. G. EDWARDS (*Chem. News*, 1920, **120**, 4—5).—Using Nernst's value in the equation for the mean molecular heat of gases,  $Cv = a + bt$ , it is shown that these linear equations are chords to the curve  $m^x = k \log T$ , where  $m = 5·95/\gamma$  or  $4 - (2\gamma/2·975)$  below or above  $\gamma = 2·975$ , from which is obtained the general equation  $m^x = k/\log T = 1/\nu \log T$ , and hence  $pv = m^x T$ ,  $m^x$  being a constant for monatomic gases.

W. G.

**Corrected van der Waals's Equation of Condition for the Quasi-diminution of the Molecule.**

E. A. HOLM (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 27, 1—33).—In the corrected van der Waals's equation an infinite series of  $b/v$  appears as the correction factor of the volume. This has been inserted by Boltzmann in an approximated form as  $1 - b/v + 0·375b^2/v^2 - 0·0369b^3/v^3$ . This cannot be true for very small volumes. The equation has been tested on Amagat's oxygen isotherms, and it is

found to be strictly applicable at pressures 250, 300, and 450 atm. and at temperatures  $0^{\circ}$ ,  $15.63^{\circ}$ ,  $99.50^{\circ}$ , and  $199.5^{\circ}$ . The negative divergence found for very high pressures is due entirely to the mathematical incompleteness of the formula. J. F. S.

**Determination of Chemical Constants.** ALFRED C. EGERTON (*Phil. Mag.*, 1920, [vi], **39**, 1—20).—The author emphasises the fact that the usual formula for the calculation of chemical constants from vapour pressures, due to Nernst, cannot give results having any theoretical significance, because the assumptions as to the specific heats at low temperatures which are contained in it have been shown to be incorrect by recent experiments. He therefore modifies the formula by substituting for these assumptions the more exact expressions for the specific heats of solids at low temperatures, and assumes that the atomic heats of gases remain constant and equal to  $5/2 \cdot R$  at the lowest temperatures. The values of the chemical constants calculated by the new formula agree, within the limits of experimental error, with those given by the formula  $-C_0 = C - 1.5 \log M$ , where  $C_0$  is a universal constant, and  $M$  is the atomic weight. The values of  $C$  obtained from the vapour-pressure formula are given in the second column below; those from the above formula in the third column:

	$C$ from vap. press.	$C$ from formula.
Mercury .....	$1.820 \pm 0.032$	1.845
Cadmium .....	$1.65 \pm 0.31$	1.468
Zinc .....	$1.23 \pm 0.26$	1.115

The value of  $C_0$  is found to be  $-1.622$ . The latent heats of vapourisation are calculated from an expression previously used (*Phil. Mag.*, 1917, [vi], **33**, 193), and found to agree with the experimental values, as well as those calculated by the equation  $\lambda = T_n 8.5 \log T_n$ , due to Nernst. The value of Stefan's constant  $\sigma$  is calculated, and found to be  $5.27 \cdot 10^{-5}$  erg. cm.<sup>-2</sup> deg.<sup>-4</sup>, which agrees with the value adopted by Planck, but is distinctly lower than the more recently determined values. J. R. P.

**Significance of the Chemical Constant and its Relation to the Behaviour of Gases at Low Temperatures.** F. A. LINDEMANN (*Phil. Mag.*, 1920, [vi], **39**, 21—25).—It is shown that the chemical constant has the dimensions of the logarithm of a pressure if the atomic heat of a monatomic gas becomes zero at the absolute zero. In this case it should be of the form  $K + 3/2 \cdot \log A + 5/2 \cdot \log \theta$ , where  $\theta$  is a characteristic constant of the substance. If the atomic heat of a monatomic gas remains  $5/2 \cdot R$  down to the absolute zero, the chemical constant has the dimensions of a pressure divided by a temperature to the power  $5/2$ , and is of the form  $K + 3/2 \cdot \log A$ . Experimental determinations show that the latter form is true within the limits of error. It follows either that  $\theta$  is very nearly equal to  $1^{\circ}$  for all substances, which seems improbable, or that the atomic heat remains constant down to the lowest temperatures. It is further shown that the chemical constant may be eliminated and the vapour pressure expressed in terms of the pressure of full radiation. It is therefore suggested that the

chemical constant may express the interaction of matter and full radiation rather than requiring that a gas can assume only a finite number of microphases, from the point of view of statistical mechanics, at a given temperature, pressure, and volume. If the value of the chemical constant could, as suggested, be derived from the radiation pressure, the quantum assumption would be avoided in the case of gases, although it would be necessary for the deduction of the law of full radiation.

J. R. P.

**Latent Heat and Surface Energy. II.** D. L. HAMMICK (*Phil. Mag.*, 1920, [vi], **39**, 32—46. Compare A., 1919, ii, 389).—On the assumption that van der Waals's constant,  $a$ , varies with the temperature, a relation is derived between the surface energy  $\rho$ , the molecular volume  $V$ , and  $a_T$ , namely,  $a_T = 6\rho V/d$ , where  $d$  is the molecular diameter. This is valid at low temperatures only. By assuming that  $a_T$  diminishes linearly with the temperature to the critical value,  $a_c$ , latent heats are calculated by Bakker's formula,  $\lambda = a_T(1/v_1 - 1/v_2)$ , for several liquids. The results are in good agreement with experimental values. The ratio  $a_T/a_c$  is found to be the same for many liquids at the boiling point, and equal to 1.4. This leads to the value of Trouton's constant. The empirical relationship between latent heat and surface energy, due to Walden, and the Eötvös-Ramsay law, can also be deduced.

J. R. P.

**Heats of Fusion, Velocities of Crystallisation, and Chemical Affinities in Crystals.** M. PADOA (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 239—243. Compare A., 1919, ii, 51, 96).—From the considerations previously developed, the conclusion is drawn that the affinity acting in the process of crystallisation should be expressed by, or at least included in, the heat of fusion of the compound, so that, under similar conditions as to molecular magnitude and structure, those compounds exhibiting the greatest velocities of crystallisation should also have the highest heats of fusion.

The melting points, heats of fusion, and velocities of crystallisation are tabulated for a number of pairs of isomorphous organic compounds, such as naphthalene and dihydronaphthalene, benzene and cyclohexane, etc. In each pair, the greater heat of fusion corresponds with the greater velocity of crystallisation characteristic of the compound containing double linkings. Further, unsaturated compounds, in general, melt at higher temperatures than the corresponding saturated compounds, this indicating the greater stability of the crystals of the former. As regards heats of fusion, the values for different series of compounds cannot be compared, the value for the saturated ethyl succinate, for instance, exceeding that for benzene; thus, the heat of fusion may be the resultant of various thermal effects, and not merely the effect of the affinity inherent to the union of the molecules in the crystal, in the same way as the heat of solution represents the algebraic sum of the various heats of ionisation, hydration, etc.

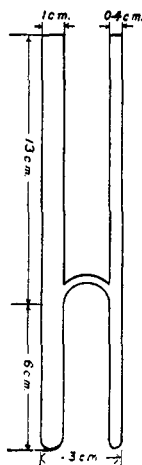
With a compound containing a triple linking, such as tolane, the velocity of crystallisation is less than that for the corresponding

isomorphous compound with a double linking (stilbene), and approaches that for the corresponding compound with a single linking (dibenzyl). The parallelism between velocity of crystallisation and heat of fusion is maintained also in this case; the melting points of compounds with triple linkings are likewise lower than those of the compounds with double linkings.

The high velocities of crystallisation shown by compounds with double linkings are explainable on the assumption that change of form on crystallisation is unnecessary with these compounds, which in the liquid state are wholly of the fumaric or wholly of the maleic type, and with the help of the latent valencies crystallise with great rapidity; on the other hand, the compounds with single or triple linkings undergo, in part at least, a preliminary transposition, which results in retardation of the crystallisation. As an instance of the influence of the molecular configuration, it may be noted that the velocity of crystallisation of dibenzyl, with which equilibrium, between the *cis*- and *trans*-forms is possible in solution, is 580 mm. per minute, whereas that of dihydrophenanthrene, which differs from dibenzyl only in the closure of the third ring, and with which no equilibrium between isomeric forms is possible, is 1200 mm. per minute.

It may be, however, that the results obtained with compounds containing the three different linkings are to be explained by the assumption that the latent valencies of the triple linking exert no action in the formation of crystals. Thomsen's thermochemical calculations ("Thermochemische Untersuchungen," 1906, 310)

show that the thermal value of a simple linking in the lower members of the paraffin series is 14.71 cal., whereas that of the double linking in the corresponding olefines is 13.27 cal., and that of the triple linking in acetylene, etc., approaches zero. T. H. P.



#### Apparatus for Determining the Melting Point of Very Hygroscopic Substances. H. J.

BACKER (*Chem. Weekblad*, 1919, 16, 1564—1565).—The apparatus consists of a narrow, thin-walled glass tube, into which the material under examination is placed, the tube being then drawn out and sealed. It communicates by means of a small, curved, lateral branch with a wider tube, in which is placed about 2 c.c. of phosphoric oxide, after which this tube is drawn out into a capillary, exhausted by means of a water-pump, and sealed. The material is thus contained in a vacuum desiccator during the determination of its melting point. W. J. W.

**Freezing-point Lowerings in Mixtures of Two Electrolytes.** K. G. DERNBY (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, 3, No. 18, 1—10).—The depression of the freezing point has been determined for aqueous solutions of mixtures of two electrolytes. The following pairs were examined: hydrochloric acid and the

chlorides of sodium, potassium, and magnesium respectively, potassium and magnesium chloride, nitric acid with potassium and magnesium nitrates respectively. The concentrations examined varied between  $0N$  and  $0.8N$ . It is shown that the freezing-point lowerings of mixtures of electrolytes with a common negative ion are always greater than the sum of the individual lowerings. For mixtures of binary electrolytes, such as  $KCl, HCl, NaCl, HCl, KNO_3, HNO_3$ , the lowering of the freezing point is approximately proportional to the concentration of the salt and of the acid. For mixtures of a ternary electrolyte and a binary electrolyte, such as  $MgCl_2, HCl, MgCl_2, KCl$ , and  $Mg(NO_3)_2, HNO_3$ , the lowering of the freezing point increases faster than the concentration. Mixtures of magnesium chloride and hydrochloric acid lower the freezing point more than mixtures of potassium chloride and magnesium chloride of the same concentration.

J. F. S.

**Calculation of the Neutral Salt Action from the Depression of the Freezing Point of Aqueous Solutions.** SVANTE ARRHENIUS and ERIK ANDERSSON (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 25, 1—9).—A theoretical paper in which, on the basis of the Arrhenius hypothesis of the mechanism of neutral salt action, an attempt is made to calculate the neutral salt action from freezing-point depressions. The osmotic pressure of a solution is strongly influenced by other substances, particularly salts; this is also true of the osmotic pressure of hydrogen ions. Since the velocity of reaction is proportional to the osmotic pressure of the surrounding substance (sucrose or ethyl acetate), and, further, the osmotic pressure of the catalyst (hydrogen ions) increases proportionally, the neutral salt action can be calculated as soon as the corresponding changes of the two osmotic pressures are known. These for the case under investigation are known from the freezing-point measurements of Dernby (preceding abstract) and from the hydrogen-ion activity determinations of Harned (*A.*, 1916, ii, 8). The calculation shows that the method is one capable of furnishing the desired result.

J. F. S.

**Simplification of the Inverse-rate Method for Thermal Analysis.** P. D. MERICA (*Bull. Bureau Standards*, 1919, No. 336, 101—104).—In plotting and recording cooling curves, the author recommends the following method, using a thermocouple, a direct-reading potentiometer and galvanometer, and two stop-watches. The watches are mounted in a single frame and held in one hand; the potentiometer is set at the desired point. When the time-temperature readings are being made, the stem of both watches is pressed at the moment the galvanometer reaches the zero, thus stopping one watch and so recording the time interval, and starting the other watch on the next interval, which is recorded in the same way. This method saves the time necessary in plotting and reading chronograph records, and does away with the use of expensive chronographs. Specimen curves for the cooling of iron made by this method are given in the paper.

J. F. S.

**Exact Formula for the Saturation Tension of Water Vapour between 0° and 50°.** PAUL SCHREIBER (*Physikal. Zeitsch.*, 1919, 20, 521—523).—The author gives the following formulæ for calculating the saturation tension of water vapour at temperatures between 0° and 50°:  $\log s = \log s_1 + \log f(T)$ , in which  $\log s_1 = p + q \log T$  and  $\log f(T)$  is a correcting factor,  $s$  is the corrected saturation tension. The values calculated by this equation are practically identical with the values given in the international meteorological tables. The values  $\log s_1 = -7.0814 + 17.8 \log (10^{-2}T)$ ,  $\log f(T) = 0.0115 - 0.0000494(T - 298)^2$  and  $\log s = -7.0699 + 17.8 \log (10^{-2}T) - 0.0000494(T - 298)^2$  are used in the calculations. J. F. S.

**Boiling Point of Liquids.** F. P. SOEBEL (*Science*, 1919, 50, 49—50).—Assuming that at the b. p. the energy of vibration of the individual molecules of a liquid and of its vapour must be equal, the author deduces the equation  $T_x = m p_x v_x / 1.49$  for a pure liquid, where  $m$  is the molecular weight and  $p_x$  and  $v_x$  the pressure and the volume of the vapour at the absolute b. p.,  $T_x$ . For ordinary liquids containing impurities, the equation becomes  $T_x = (p_x v_x - C)m / 1.49$ , where  $C$  is a constant characteristic of each liquid. In the case of water ( $m = 18$ ;  $C = 8.7$ ), the calculated values of  $T_x$  at 273°, 313°, and 473° (abs.) are 270°, 313.3°, and 473.5° respectively. Similar agreement is found in the case of other liquids in which association does not occur. CHEMICAL ABSTRACTS.

**Vapour Pressure and Free Energies of the Hydrogen Haloids in Aqueous Solution. The Free Energy of Formation of Hydrogen Chloride.** STUART J. BATES and H. DARWIN KIRSCHMAN (*J. Amer. Chem. Soc.*, 1919, 41, 1991—2001).—Determinations have been made of the vapour pressures of hydrogen chloride, hydrogen bromide, and hydrogen iodide above their aqueous solutions between the concentrations 3.2 and 10.0*N*, 5.8 and 11.0*N*, and 6.0 and 9.7*N*, respectively, at 25°, and of hydrogen chloride between 5.5 and 9.2*N* at 30°. By the method employed, which consisted in determining the hydrogen haloid contained in a given quantity of air or nitrogen in equilibrium with its solution, and comparing this with the amount of aqueous vapour which the same air contained when in equilibrium with pure water at the same temperature, partial pressures as small as 0.001 mm. were determined with an accuracy of a few per cent. The vapour-pressure measurements of hydrochloric acid solutions between 3.2*N* and 7.15*N* are in good agreement with the *E.M.F.* data for hydrochloric acid concentration cells. The free energy of formation of hydrogen chloride at 25° is -22,700 cal. The free energies of formation of the halogen acids at various concentrations, 0.1—11.0 mols. per litre, in aqueous solution are given in a table in the paper. J. F. S.

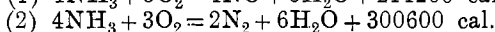
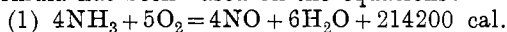
**Constant Temperature Still-head for Light Oil Fractionation.** FREDERICK M. WASHBURN (*J. Ind. Eng. Chem.*, 1920, 12, 73—77).—The apparatus described consists of two essential



parts, namely, a Hempel column and a constant temperature still-head of the type suggested by F. A. Brown (T., 1880, **37**, 49). This still-head is a spiral of about 6 inches diameter made from 12 feet of  $\frac{3}{8}$  inch iron tube; it is surrounded by an oil-bath, which is provided with a stirrer and maintained at the required temperature by a coil of resistance wire, thermo-regulator, relay, etc. The lower end of the spiral is connected with the side-tube of the Hempel column, whilst the upper end is fitted with a thermometer pocket and a side-tube leading to an ordinary condenser. W. P. S.

**Heat of Formation Calculated from the Wave-length of Absorption Bands.** A. L. BERNOUILLI (*Helv. Chim. Acta*, 1919, **2**, 720—728).—The author has deduced an expression, whereby from the absorption bands corresponding with characteristic ultra-violet electron vibrations the heat of formation of a compound from its elements may be calculated. This expression for a binary compound has the form  $Q = 0.01128[(\sqrt{\Theta_1/\alpha v_1^{\frac{2}{3}}} - \sqrt{\Theta_2/\beta v_2^{\frac{2}{3}}}) - \sqrt{\Theta'/(\alpha + \beta - \delta)v'^{\frac{2}{3}}}]$ , in which  $Q$  is the heat of formation,  $v_1$ ,  $v_2$ , and  $v'$  the atomic volumes of the constituent elements and the molecular volume of the compound respectively;  $\Theta_1$ ,  $\Theta_2$ , and  $\Theta'$  are the melting points, in absolute degrees, of the elements and the compound respectively,  $\alpha$  and  $\beta$  are the electron numbers or valencies of the elements, and  $\delta$  is the number of charges given up in the formation of the molecule. This formula is tested in the case of a number of binary compounds, and the results compared with the experimental values. The two sets of results are remarkably close; for example, carbon dioxide, calc. 108.3, obs. 106.0; silver chloride, calc. 29.05, obs. 29.0. J. F. S.

**Heat of Reaction of Ammonia Oxidation.** GUY B. TAYLOR (*J. Ind. Eng. Chem.*, 1919, **11**, 1121—1123).—The temperature most favourable to the catalytic oxidation of ammonia by means of air is 800°. In order to determine the amount of external energy required to maintain the catalyst at the optimum temperature a formula has been based on the equations:



The temperature rise is expressed by the formula  $t = Q/C$ , where  $Q$  represents the heat of reaction in calories, and  $C$  the specific heat of the products of the reaction. From 0° to 800° water-vapour is the only gaseous product with an appreciable temperature-coefficient, and this may be taken as 8.34. In the following formula,  $t^\circ = (75150x - 21600y)/(7.08 + 3.41x - 0.25y + 8.34V/B - V)$ ,  $V$  represents the partial pressure of water-vapour,  $B$  the total pressure of the air-ammonia-water vapour mixture,  $x$  the molecular fraction of ammonia in the mixture, and  $y$  the molecular fraction of nitric oxide produced in the oxidation. For maintaining the catalyst at the right temperature, pre-heating the mixture, electric heating, or enriching the current of ammonia and air with oxygen have been shown to give equally satisfactory results. C. A. M.

**Critical Densities of Hydrogen, Helium, and Neon.** J. J. VAN LAAR (*Chem. Weekblad*, 1919, **16**, 1557—1564).—In the cases of hydrogen and helium the extrapolated values for  $D_c$  obtained from the curve  $\frac{1}{2}(D_1 + D_2) = f(T)$  are found to be too high. Thus the figure 0.0310 so obtained for hydrogen would correspond to  $\gamma = 0.46$ , which is an impossible value. The author calculates that for hydrogen  $D_c = 0.0287$ , and for helium  $D_c = 0.0598$  instead of 0.066 as given by the curve.

In the case of neon there is agreement between the extrapolated value and the calculated figure,  $D_c$  being 0.456. W. J. W.

**The "Density Numbers" of Groshans.** W. P. JORISSEN (*Chem. Weekblad*, 1917, **14**, 1066—1071).—The volume in c.c. of 1 gram of a vaporised substance at the boiling point is given by the expression  $82T_{b.p.}/M$ , where  $M$  is the molecular weight. Elimination of  $T_{b.p.}$  between this expression and the boiling point formula of Groshans,  $T_{b.p.} = 27.8M\sqrt{x}/n$ , gives the vapour volume in c.c. of 1 gram  $2280\sqrt{x}/n$ .  $x$  is a constant for the class of substances considered, and  $n$  is the sum of the density numbers of the elements involved (*Ann. Phys. Chem.*, 1849, **78**, 116). For the elements carbon, hydrogen, and oxygen the density numbers are unity, and  $n$  is therefore the number of atoms in the molecule. For other elements  $n$  is greater than unity. For unassociated liquids the expansion in the transition from liquid to vapour is  $570\sqrt{x}$ . By comparing this formula with the expansion determined experimentally by Masson (A., 1891, 379) for methyl, ethyl, propyl, phenyl, butyl, and amyl chlorides,  $x$  is determined for each, and the density number for chlorine is determined from the boiling-point formula. The values found range from 3.40 to 4.44. The value given by Groshans is 4. W. S. M.

**Determination of Avogadro's Normal Volume  $V_A$  and of the Atomic Weights of Hydrogen, Helium, and Argon.** J. J. VAN LAAR (*Chem. Weekblad*, 1919, **16**, 1243—1250).—A continuation of a previous communication (A., 1919, ii, 461).

The most probable value of  $V_A$  is considered to be  $22415^3$  c.c. The atomic weights of hydrogen, helium, and argon are stated to be 1.007697 ( $=1.00770$ ), 3.9998 ( $=4.000$ ), and 39.95 respectively.

W. J. W.

**Molecular Attraction. III. The Characteristic Equation.** K. K. JÄRVINEN (*Ann. Acad. Sci. Fennicae*, 1919, [A], **12**, Reprint 44 pp.).—A continuation of the theoretical discussion on molecular attraction (compare A., 1913, ii, 293; A., 1915, ii, 251). The internal pressure,  $p_a$ , is calculated by the equation  $p = RT/V.f - p_a$ , on the basis of the law of molecular attraction  $F = km^2/r^5$ . It is found that  $p_a = a/v^3$  for monatomic substances, and  $p_a = a/\{v^3(v^{\frac{1}{3}} - 0.242b)^5\}$  for polyatomic substances, where  $a$  and  $b$  are the constants of van der Waals's equation. It is thus much smaller than that calculated from the latter equation. The critical pressure,  $p_c = RT/V.f$ , is also calculated, and thence a table of values of  $f$

deduced, which may be used to find the deviations from the ideal state. Values of  $f$  are also calculated from the equations  $f = p - p_a / RT \cdot v$  and  $f = dp/dt \cdot v/R$ , the latter obtained by differentiation of the characteristic equation. These agree approximately with the theoretical values. The differences are taken to mean that the theory is yet incomplete. It is also found that  $b$  decreases with temperature, but this need not in reality be the case. The pressure, the critical data, and the values of  $v_k/b_0$ ,  $RT/pv_k$ ,  $dp/dt \cdot v/R$ , and  $dp/dt \cdot T/p$ , may be obtained with fair approximation. Only approximate accuracy is claimed.

J. R. P.

### Effects of Acids and Bases on the Surface Energy Relations of $\beta\beta'$ -Dichloroethyl Sulphide (Mustard Gas).

WILLIAM D. HARKINS and D. T. EWING (*J. Amer. Chem. Soc.*, 1919, **41**, 1977—1980).—The surface tension between  $\beta\beta'$ -dichloroethyl sulphide and a number of liquids has been determined with the object of finding a suitable emulsifying agent for the preparation of aqueous emulsions of this substance. The following values of the surface tension in dynes per cm. have been found between  $\beta\beta'$ -dichloroethyl sulphide and the liquids named: water, 28.36; 0.1*N*-hydrochloric acid, 28.90; 0.1*N*-sodium hydroxide, 12.78; 0.1*N*-sodium carbonate, 18.82; 1% solution of turkey-red oil, 14.47; 1% solution of turkey-red oil in 0.1*N*-sodium carbonate, 8.35; 1% Twitchell's solution, 12.32; 1% Twitchell's solution in 0.1*N*-sodium carbonate, 12.89; 1% maize oil solution, 12.94; and 1% maize oil in 0.1*N*-sodium carbonate, 10.91. The surface tension of several organic liquids has also been measured: *aa*-diphenylpropane, 20°, 37.15, 25°, 36.64; *aa*-diphenylethane, 20°, 37.67, 25°, 37.20; diphenylmethane, 20°, 37.56; ditolylmethane, 20°, 35.51, 25°, 34.80; propylbenzene, 20°, 32.22, 25°, 31.30. All determinations were made by the drop-weight method.

J. F. S.

**Viscosity of Pure Liquids.** SVANTE ARRHENIUS (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 20, 1—40).—A theoretical paper, in which a large volume of work on the viscosity of liquids is discussed and correlated. It is shown that the ratio  $\eta_b \times 10^5 : \sqrt{s}$  is approximately constant for non-associated organic liquids. The symbols have the significance,  $\eta_b$  is the viscosity of a liquid at the boiling point and  $s$  is the density, and the constant varies between 230 and 320. The constant is not obtained in the case of a few liquids, which are characterised by the fact that the expression  $K_1 = T^2(d \log \eta / v^3) / dt$  does not show a minimum below the boiling point. These liquids are ethylene, propylene, and *iso*-butylene bromides, benzene, and carbon tetrachloride. The presence of negative atoms, such as the halogens, sulphur, or oxygen, increases the value of the ratio  $\eta_b : \sqrt{s}$ . The influence of pressure on the viscosity is nearly represented by a linear equation  $\log \eta_p = \log \eta_0 + l(p - p_0)$ , where  $\eta_0$  is the viscosity at the external pressure zero (practically atmospheric pressure),  $p$  is the total pressure (external and internal) calculated according to van der Waals's

theory, and  $p_0$  the internal pressure at zero external pressure. The influence of temperature on viscosity may, for non-associated liquids, be expressed by the formula  $d \log \eta \cdot v^{1/3} / dt = K_1 / T^2$ .  $K_1$  is nearly proportional to the absolute boiling point  $T_b$ , so that  $K_1 : T_b$ , if ordinary logarithms are used for calculating  $K_1$ , does not change for normal organic liquids between greater limits than 1—1.2. Benzene and the liquids named above are exceptions. For associated liquids the ratio  $K_1 : T_b$  possesses higher values, between 1.25 and 4.32. There is a pronounced parallelism between the values of the ratios  $\eta_b : \sqrt{s}$  and  $K_1 : T_b$ . In an homologous series,  $K_1 : T_b$  generally increases with the boiling point. There is a great analogy between the effect of temperature on the vapour pressure and on the product of the viscosity and the specific volume. J. F. S.

**Investigations concerning the Viscosity of Binary Liquid Mixtures.** HANS EGNÉR (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 22, 1—13).—A theoretical paper in which a large number of viscosity determinations of various authors are collected and examined in connexion with the modified logarithmic formula of Arrhenius,  $\log \eta = n_1 \log \eta_1 + n_2 \log \eta_2$ , where  $\eta_1$  and  $\eta_2$  are the viscosities of the components of the mixtures, and  $n_1$  and  $n_2$  the molecular concentrations. It is shown that this formula represents the variation of the viscosity in binary liquid mixtures more exactly than any other formula. J. F. S.

**Theoretical Significance of Viscosity Measurements of Colloidal Solutions.** SVANTE ARRHENIUS (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 21, 1—22).—A theoretical paper in which a large number of viscosity determinations of colloidal solutions are discussed. It is shown that Einstein's viscosity formula is fully established by Bancelin's results (A., 1911, ii, 586, 1067) as soon as the logarithmic formula

$$\log \eta - \log \eta_0 = \theta \phi$$

is employed. The proposed extension of Einstein's formula put forward by Smoluchowski is not confirmed by Oden's measurements on colloidal sulphur (A., 1913, ii, 485). J. F. S.

**Viscosimeter for Measuring Viscosities and Fluidities.** GEORGES BAUME and HENRI VIGNERON (*Ann. Chim. anal.*, 1919, [ii], **1**, 379—383).—The viscosimeter tube consists of a capillary provided with a bulb at its upper end and a short length of wide tube at its lower end; this tube is fixed vertically by means of a cork in a test-tube containing 20 c.c. of the oil under examination, the lower end of the tube being immersed in the oil up to a mark just below the capillary. A thermometer passes through a T-piece carried by the cork, the bulb of the thermometer dipping into the oil. The test-tube is inserted in a boiling bulb provided with a reflux apparatus. This boiling bulb may contain ether, acetone, benzene, or water, according to the temperature at which the viscosity is to be determined; when the required temperature has

been reached, the oil is forced upwards into the viscosimeter tube by a pressure ball attached to a branch of the T-piece; the pressure is then released, and the time taken for the level of the oil to fall from a mark just above the bulb (on the viscosimeter tube) to one just below it is noted.

W. P. S.

### **Emulsification by Adsorption at an Oil-Water Interface.**

S. E. SHEPPARD (*J. Physical Chem.*, 1919, **23**, 634—639).—Emulsions of nitrobenzene in sulphuric acid and hydrochloric acid may be readily prepared by making the acid of the same density as the nitrobenzene. Similar moderately stable emulsions were prepared by saturating the acid (sulphuric) with lead sulphate or calcium sulphate, or hydrochloric acid with sodium chloride or lead chloride, in both cases the acid being of the same density as the nitrobenzene. It therefore appears that, in accordance with Bancroft's general theory of peptisation, adsorption at a liquid-liquid interface is capable of effecting emulsification. The systems thus produced, on ageing, pass into a condition approaching Pickering's emulsions, but with a great diminution of the dispersity.

J. F. S.

**Nature of Osmotic Pressure.** MITSUJI KOSAKAI (*Proc. Soc. Expt. Biol. Med.*, 1919, **16**, 118—119).—The hæmolytic effects of formaldehyde and carbamide were found to be, like that of boric acid, the result of osmotic pressure. The rates of diffusion of boric acid, formaldehyde, and carbamide are 90 sec., 30 sec., and less than 5 sec. respectively. These differences correspond with the differences in the hæmolytic action of the three substances, and confirm the view that osmotic pressure is not a direct property of a solute, but is merely water pressure developed by the process of diffusion.

CHEMICAL ABSTRACTS.

### **Osmotic Pressure. II. The Nature of Osmotic Pressure.**

MITSUJI KOSAKAI (*J. Immunology*, 1919, **4**, 49—65).—The same degree of osmotic hæmolysis is not produced by identical concentrations of boric acid, formaldehyde, and carbamide, or by a corresponding lowering in the medium of suspension of the treated corpuscles. As the treating concentration of the three hæmolytic substances is correspondingly diminished, the ratio between that concentration and the final concentration, in the hæmolytic experiment, increases disproportionately with the different substances. The osmotic hæmolysis of corpuscles which have been treated with the three hæmolytic substances in the same osmotic concentration is not inhibited by identical concentrations of sodium chloride or of the hæmolytic substances themselves. All these facts contradict the assumption that osmotic pressure is exerted directly by the solute. Osmotic pressure is not a direct property of a solute, but is solely the pressure exerted by water which has passed, by the unexplained process of diffusion, through a semipermeable membrane to the side of the higher osmotic concentration.

CHEMICAL ABSTRACTS.

**Osmotic Pressure of an Electrolyte.** OSKAR KLEIN (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, 5, No. 6, 1—9).—A mathematical paper in which an expression is deduced showing the connexion between osmotic pressure, concentration, temperature, and dielectric constant. The reasoning is based on thermodynamical and mechanical (kinetic) principles, and is simpler than that used by Milner (*A.*, 1913, ii, 481) in a similar problem. T. S. P.

**The Diffusion of Electrolytes into Jellies. II. The Dependence of the Diffusion on the Mobility of the Ions and the Hydration and Polymerisation of the Molecules.** OTTO VON FÜRTH and FRANZ BUBANOVIĆ (*Biochem. Zeitsch.*, 1918, 92, 139—170. Compare *A.*, 1919, ii, 13).—Diffusion in jellies differs in most cases from free diffusion in aqueous solution, and is dependent on the character of the jelly. The velocity with which acids, bases, and polymerised salts penetrate jellies is smaller than would be expected from the mobility of their ions. Weakly hydrated salts show normal diffusion (diffusion similar to that in aqueous solution) in jellies. Strongly hydrated salts, on the other hand, contrary to their behaviour in aqueous solution, diffuse relatively faster than in the previous case, so that their diffusion velocity approximates to the theoretical value obtained from the mobility of the ions. S. S. Z.

**Influence of the Concentration of Electrolytes on the Electrification and the Rate of Diffusion of Water through Collodion Membranes.** JACQUES LOEB (*J. Gen. Physiol.*, 1919, 20, 173—199).—When an aqueous solution is separated from pure water by a collodion membrane, the initial rate of diffusion of water into the solution is influenced in an entirely different way by solutions of electrolytes and of non-electrolytes. The latter influence the rate of diffusion in direct proportion to their concentration, and this effect is termed the gas-pressure effect. Solutions of electrolytes show the gas-pressure effect also, but it commences at a somewhat higher concentration than in the previous case. If the concentration of the electrolyte is below that at which the gas-pressure effect is observed, the solutions have a specific influence on the initial rate of diffusion, which is not found in the case of the solutions of non-electrolytes, and is due to the diffusion of the water in an electrified condition, the sign of the charge depending on the nature of the electrolyte in solution, according to the theory which has been advanced by the author (*A.*, 1919, ii, 497). In these lower concentrations, the curves representing the influence of the concentration of the electrolyte on the initial rate of diffusion of water into the solution show that, within a range of concentrations between  $M/256$  and  $M/16$  or more (according to the nature of the electrolyte), the reverse of what should be expected on the basis of van't Hoff's law is noticed, namely, that the attraction of a solution of an electrolyte for water diminishes with an increase in concentration. Whilst no definite assumption concerning the

origin of the electrification of water and the mechanism by which the ions influence the rate of diffusion of water particles through collodion membranes is made, it is suggested that in the lowest concentrations, attraction of the electrified water particles by the ions with the opposite charge prevails over the repulsion of the water particles by ions with the same sign of charge, whilst beyond a certain critical concentration the repelling action of the ion with the same charge as that of the water particles on the latter increases more rapidly with increasing concentration of the solute than the attractive action of the ion with the opposite charge.

It is shown that negative osmosis is due to the repulsion of the electrified particles of water by the ion with the same charge as that borne by the water.

J. C. D.

**The Effect of Strain on Solubility.** J. C. HOSTETTER (*Science*, 1919, 50, 25).—It is possible that fluctuating temperature and, perhaps, some indirect effects brought about by pressure may account for the solidification of crystals compressed in contact with their solution by loosely fitting pistons, as found by James Thomson, Le Chatelier, and Spring, without the necessity of postulating large increases in solubility due to non-uniform pressure. In preliminary experiments, individual crystals were subjected to stress at constant temperature by direct loading, and the effect on the concentration of the surrounding solution was studied by measuring the electrical conductivity. No change in concentration was found. The test was sufficiently sensitive to indicate that the effect of non-uniform pressure is much less than that produced by the same pressure acting uniformly. However, in another series of experiments, in which an unloaded crystal was placed alongside a loaded crystal, the former grew at the expense of the latter, showing that a very slight increase of solubility was produced by the stress. The method of loading the crystals has a large influence on the effects found, thus indicating the importance of the stress distribution. The experiments of Becker and Day on the linear force of growing crystals are cited as indicating the stability of a crystal in its solution, even when subjected to pressure. In their experiments, loaded crystals were found to lift the load during growth, although the pressures on the supporting edges of the crystals were finally of the order of magnitude of the crushing strength of the crystal. The evidence so far obtained indicates that the effect of strain on solubility is a second-order effect.

CHEMICAL ABSTRACTS.

**Influence of Electrolytes on Solubility.** EBBE LINDE (*Arkiv. Kem. Min. Geol.*, 1917, 6, No. 20, 1—17).—The solubility of ethyl ether and ethyl acetoacetate has been determined in water and in solutions of certain electrolytes. In the case of ethyl ether, it is found that 7.88 grams dissolve in 100 c.c. of water at 18°. The influence of mixtures of two electrolytes on the solubility of ether in water is determined for the pairs of electrolytes, sodium

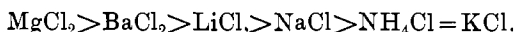
sulphate-sulphuric acid, sodium sulphate-sodium hydroxide, and sodium chloride-sodium acetate. In the first two pairs, the total electrolyte concentration was  $0.5N$ , and in the last pair  $N$ . The concentrations of the two electrolytes were varied within these limits. For the pair of electrolytes, sodium sulphate-sulphuric acid, it is shown that the solubility is 5.52 grams per 100 c.c. of  $0.5N$ -sodium sulphate, and rises regularly with decreasing sodium sulphate concentration and increasing sulphuric acid concentration to 7.72 grams per 100 c.c. of  $0.5N$ -sulphuric acid. In  $0.5N$ -mixtures of sodium sulphate and sodium hydroxide, the solubility is constant, 5.53 grams per 100 c.c. of solution, whilst in the case of sodium chloride and sodium acetate the solubility is 4.62 grams in 100 c.c. of  $N$ -sodium chloride, and falls regularly to 3.44 grams in 100 c.c. of  $N$ -sodium acetate. The electrolytes are seen, therefore, to have an additive effect. The solubility is also determined in solutions of sodium acetate and sodium chloride of varying concentration, and in both cases shown to increase steadily with increasing dilution, but in neither case is the depression of the solubility in keeping with Steiner's expression. Both sets of solubility values are fairly in keeping with the expression of Hoffmann and Langbeck (A., 1905, ii, 374). The solubility of ethyl acetoacetate has been determined in water, and solutions of sodium chloride and sodium nitrate of various concentrations at  $16-16.5^{\circ}$ . It is shown that 100 c.c. of water dissolve 12.5 grams of ethyl acetoacetate at  $16-16.5^{\circ}$ . In  $N$ -sodium chloride, 8.4 grams dissolve in 100 c.c., and this value increases with decreasing concentration of sodium chloride, but the solubility change is in keeping with neither of the above expressions. In sodium nitrate solution, 11.4 grams of ethyl acetoacetate dissolve in 100 c.c. of  $N$ -sodium nitrate, and the solubility increases in accordance with both the above-named expressions on decreasing the nitrate concentration. The addition of alcohol to solutions of sodium chloride and nitrate increases the solubility of ethyl acetoacetate in these solvents.

• J. F. S.

**Contrasting Effects of Chlorides and Sulphates on the Hydrogen-ion Concentration of Acid Solutions.** ARTHUR W. THOMAS and MABEL E. BALDWIN (*J. Amer. Chem. Soc.*, 1919, **41**, 1981—1990).—The hydrogen-ion concentration of a chrome tanning liquor has been determined in the presence of various concentrations of sodium chloride, ammonium chloride, sodium sulphate, ammonium sulphate, and magnesium sulphate. The effect of the addition of chlorides is to increase the hydrogen-ion concentration, whilst that of sulphates is to decrease it, although, on keeping, the concentration increases somewhat. Similar experiments were carried out with pure chromium sulphate solution, chromium chloride solution, sulphuric acid ( $0.0005N$ ), hydrochloric acid ( $0.004N$ ), sulphuric acid ( $0.1N$ ), and hydrochloric acid ( $0.1N$ ), using a number of chlorides and sulphates. In every case, the chlorides are found to increase the hydrogen-ion concentration, and



the sulphates to reduce it. The power of increasing the hydrogen-ion concentration follows the order



J. F. S.

**Degree of Ionisation of Very Dilute Electrolytes.** GILBERT N. LEWIS and GEORGE A. LINHART (*J. Amer. Chem. Soc.*, 1919, **41**, 1951—1960).—A theoretical paper in which the authors deduce a general equation for the freezing-point lowering of dilute strong electrolytes. This equation has the form  $n\lambda - \theta/c = \beta c^\alpha$ , in which  $n$  is the number of dissociated parts,  $\lambda$  the degree of dissociation,  $\theta$  the lowering of the freezing point,  $c$  the concentration, and  $\beta$  and  $\alpha$  characteristic constants. The calculation and observed values of  $\theta$  for fourteen salts at a series of concentrations are compared and shown to be in good agreement. The thermodynamic degree of dissociation is calculated for the same salts over a range of concentration  $10^{-1}$ — $10^{-8}N$ . The constants  $\alpha$  and  $\beta$  of the above equation can be obtained from freezing-point determinations. The calculated degree of dissociation diverges extraordinarily from the value obtained by the usual method.

J. F. S.

**The Influence of the Dielectric Constant of the Solvent and of the Electric Energy of the Ions on Electrolytic Dissociation.** MARIO BASTO WAGNER (*Anal. Fis. Quim.*, 1919, **16**, 229—257).—A purely mathematical paper.

W. S. M.

**Mechanism of Electrolytic Dissociation.** B. CABRERA (*Anal. Fis. Quim.*, 1918, **16**, 186—225).—A mathematical paper developing the theory that the ions resulting from the solution of a crystalline substance are already present as such in the crystal, the formation of neutral molecules being thus subsequent to the act of solution or fusion.

W. S. M.

**Atomic Constitution of a Crystal Surface.** E. MADELUNG (*Physikal. Zeitsch.*, 1919, **20**, 494—496).—A mathematical paper in which the author considers the condition of the surface layer of molecules in crystals of the sodium chloride type. It is shown that in crystals of the regular type, consisting of binary compounds, the atoms of one kind on the surface are displaced in directions at right angles to the surface with respect to the atoms of the other kind. The displacement decreases in the body of the crystal according to a simple exponential equation. It is also shown that, since the atoms of electrolytes carry electric charges, an electric double layer must, in consequence of the displacement, surround the crystal surface.

J. F. S.

**A New Method of Electrical Synthesis of Colloids.** THE SVEDBERG (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 10, 1—18).—The author has prepared gold and silver sols of high dis-

person by a modified method. The apparatus consists of a quartz tube in which a small hole about 1 mm. diameter is bored. The metal electrodes, gold or silver, pass down this tube, and are so placed that the arc may be formed opposite the hole. The quartz tube is so arranged that a current of nitrogen passes through it both from the top and the bottom. The quartz tube is placed in an outer glass jacket containing about 30 c.c. of the dispersion medium (alcohol), and this jacket is surrounded by a further jacket containing a cooling agent (ice and salt or solid carbon dioxide and alcohol). An electromagnet is placed with its poles on either side of the small hole in the quartz tube. The current (1 amp. 220 volts) is switched on, and an arc of the usual type appears for about a second, then, owing to a melting of the lower electrode (anode), the quartz tube becomes somewhat stopped up, and so the electrode is protected from the dispersion medium; the arc becomes a sharp-pointed flame, and this is drawn through the hole in the tube by the action of the magnet. Metallic clouds appear and are absorbed by the dispersion medium. The appearance of the arc has been examined spectrographically in both conditions and the differences noted. The author holds that the condensation of metal vapour is the cause of the sol formation. Other forms of apparatus are described in the paper.

J. F. S.

**Colloid Metal Reactions. Spectrum Analysis and Blood Colouring Matter.** EDUARD RICHTER (*Kolloid. Zeitsch.*, 1919, **25**, 208—211).—A number of colloid reactions between 1% gold chloride solution and 1:1000 solutions of adrenaline, alloxan, tannic acid, and *p*-phenylenedimethyldiamine are described. In each case, colloidal gold is produced, but of different degrees of dispersity. From the experiments, it is deduced that certain diamines possess a particularly powerful reducing action, and are probably to be classified with the reducing substances of the amino-group which occur in the animal organism. Certain hydroxy-substances also show a similar reducing action.

J. F. S.

**Colour of Colloids. IX.** WILDER D. BANCROFT (*J. Physical Chem.*, 1919, **23**, 554—571. Compare A., 1919, ii, 500).—A continuation of the previous discussion. It is shown that with very small particles, the light which is ordinarily reflected selectively is transmitted by resonance, whilst the light which is ordinarily transmitted is scattered. Massive gold is red by multiple reflection, and thin films are green by transmitted light. Very small particles reflect green and transmit red light. Massive gold reflects yellow when compact, and brown to black when porous. Particles which do not resonate are yellow or brown by reflected light and transmit blue light. Silver is yellow by multiple reflection, and thin films are blue to green by transmitted light. Very small particles reflect blue and transmit yellow. Particles which do not resonate transmit blue light and reflect red. Colloidal indigo solutions transmit red light, and the surface colour of indigo is red. Sodium fog scatters

blue light and transmits the yellow, which the vapour absorbs. Iodine fog scatters red light. J. F. S.

**Colours of Colloids. X.** WILDER D. BANCROFT (*J. Physical Chem.*, 1919, **23**, 603—633. Compare A., 1919, ii, 500).—A continuation of the previous discussion. In the present paper the colours of glasses and glazes are considered. It is shown that in glasses and glazes, gold, silver, copper, platinum, iridium oxide, selenium, tellurium, sulphur, lead antimonate, carbon, magnetite, ferric oxide, stannic oxide, zirconium oxide, arsenious oxide, titanium oxide, and calcium phosphate occur usually as a second phase. Chromium occurs in some form as a second phase in chrome Aventurine glass and copper in Egyptian blue. Some glasses coloured by iron, chromium, manganese, and cobalt are optically empty. In enamels the substance causing the colour is probably chiefly adsorbed by the material causing the opacity. J. F. S.

**Colours of Colloids. XI.** WILDER D. BANCROFT (*J. Physical Chem.*, 1919, **23**, 640—644. Compare preceding abstract).—A continuation of the previous discussion. In the present paper the colours of gem stones are considered. J. F. S.

**Coagulation.** ARNE WESTGREN (*Arkiv. Kem. Min. Geol.*, 1918, **7**, No. 6, 1—30).—The coagulation of gold sols has been examined with the object of ascertaining the influence of the size of the colloidal particles, the nature of the coagulating ions, and the temperature on the velocity of the slow coagulation. Forty c.c. of the sol were mixed with 10 c.c. of an electrolyte, and after definite intervals of time had elapsed 5 c.c. of the mixture were withdrawn and run into 25 c.c. of 0.5% gelatin solution and the particle concentration determined. Using sols with particles of radius 120  $\mu\mu$ , 77  $\mu\mu$ , and 49  $\mu\mu$  respectively, it is shown that the velocity of coagulation is independent of the size of the particles. Using the following electrolytes to coagulate the sols (hydrochloric acid, sodium, lithium, potassium and rubidium chlorides, sodium hydroxide, and sodium iodate), it is shown that the ionic conductivities of the ions are determinative of the coagulating power. Thus hydrochloric acid, the cation of which has the greatest ionic conductivity, is the most active coagulator of all the chlorides, whereas lithium chloride with its slow-moving cation is the least active. Potassium chloride and rubidium chloride, which have cations of about the same ionic conductivity, have about the same coagulating power. Since gold sols are negative colloids, it follows that when they are coagulated by cations the anions must exercise a stabilising influence, and this is shown in the coagulation by sodium derivatives, for sodium hydroxide, with its rapidly moving hydroxyl ion, is the least efficient coagulator, whilst sodium iodate with its slow-moving anion is the most efficient coagulator. Using hydrochloric acid and sodium chloride at various temperatures, it is shown that the velocity of coagulation does not depend on the temperature only, because the

Brownian movement of the particles depends on it, but also because the specific coagulation power of the electrolytes changes with the temperature.

J. F. S.

**Effect of the Wall of Vessels on the Velocity of Gaseous Reactions.** ELICHI YAMAZAKI (*J. Tokyo Chem. Soc.*, 1919, 40, 606—608).—This is a theoretical paper, attempting to give an explanation for Kooij's work (A., 1893, ii, 569), in which the velocity of dissociation of phosphine was shown to be affected by the nature of the vessel, the ratio of the velocity in the new vessel to that in the old being 1 : 2.25. According to the author, the decomposition of phosphine in a vessel should be considered to be a heterogeneous chemical reaction, that is, (1) a formation of the diffused zone between gas and vessel, (2) chemical reaction. In the new vessel the wall becomes the "diffusion zone," but in the old vessel the decomposition product (phosphorus) adheres to the surface of the vessel, thus creating a larger surface which accelerates the velocity of the diffusion. Ordinarily the velocity of the diffusion of the gas over the wall is so fast that only the velocity of the chemical reaction is measured as the total reaction velocity. The author believes that the vessel acts as a catalyst in the same manner as platinum black or sponge, by removing the product of the reaction, thus maintaining general equilibrium. More detailed investigation and explanation are promised. CHEMICAL ABSTRACTS.

**An Unsolved Problem in the Application of the Quantum Theory to Chemical Reactions.** W. C. M. LEWIS (*Phil. Mag.*, 1920, [vi], 39, 26—31).—On applying the quantum theory to a unimolecular reaction, it is shown that very different results are obtained according as it is assumed that the absorption of radiation is continuous or discontinuous. A very large discrepancy exists in both cases between the calculated and observed velocity constants, which is much greater on the discontinuous view than on the continuous. This discrepancy is always in the sense that the observed velocity constant is many times greater than the calculated; on the hypothesis of continuous absorption, the observed constant is of the order of  $10^7$  times greater than the calculated, and also appears to be independent of temperature, for different reactions. The explanation of this discrepancy is expected to throw light on the theory of physicochemical processes.

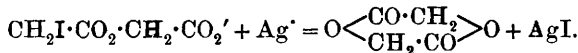
J. R. P.

**The Propagation of Flame in Mixtures of Methane and Air. I. Horizontal Propagation.** WALTER MASON and RICHARD VERNON WHEELER (T., 1920, 117, 36—47).

**The Propagation of Flame in Complex Gaseous Mixtures. IV. The Uniform Movement of Flame in Mixtures of Methane, Oxygen, and Nitrogen. "Maximum-speed Mixtures" of Methane and Hydrogen in Air.** WILLIAM PAYMAN (T., 1920, 117, 48—58).

**Hydrolysis of Iodoacetic Acid.** BROR HOLMBERG (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 11, 1—12).—The velocity of replacement of iodine by hydroxyl in the sodium and barium salts of iodoacetic acid by the action of sodium and barium hydroxides has been studied; the influence of neutral salts (sodium chloride and iodide and barium chloride) was also investigated. The reaction is bimolecular, its velocity being intermediate between those observed for the corresponding bromo- and chloro-acids (compare Johansson, A., 1912, ii, 544). Contrary to expectation, therefore, iodoacetic acid is more stable than bromoacetic acid (compare Drushel and Simpson, A., 1918, i, 57). The effect of the concentration of the metal ions on the velocity constant,  $C$ , is given by the equations  $C = 0.106[\text{Na}']^{0.1}$  and  $C = 0.220[\text{ba}]^{0.2}$ , where  $\text{ba} = \frac{1}{2}\text{Ba}$ .

The reaction between iodoacetic acid or its salts and silver nitrate was also studied. The formation of silver iodide takes place much more quickly than the production of acid, and the author concludes that the most important reactions are represented by the equations:  $2\text{CH}_2\text{I}\cdot\text{CO}_2' + \text{Ag}^+ = \text{CH}_2\text{I}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CO}_2' + \text{AgI}$  and



If the solutions are not too dilute, the formation of iodoacetylglycollic acid takes place much more quickly than the formation of glycollic acid. Glycollic acid is then formed indirectly, or it may also be formed directly, according to the equation  $\text{CH}_2\text{I}\cdot\text{CO}_2' + \text{Ag}^+ + \text{H}_2\text{O} = \text{OH}\cdot\text{CH}_2\cdot\text{CO}_2' + \text{H}^+ + \text{AgI}$ .  
T. S. P.

**Effect of Chlorine on Periodic Precipitation.** [Miss] A. W. FOSTER (*J. Physical Chem.*, 1919, **23**, 645—655).—When silver nitrate is allowed to diffuse into gelatin films containing potassium chromate, a series of concentric rings is formed, the spacing of which decreases with the distance from the centre. The appearance and spacing of these rings does not depend on the time which has elapsed between the formation of the gelatin film and the addition of the silver nitrate. If, however, a trace of chloride is present in the gelatin the appearance is altered. Making up the gelatin chromate solution with tap water is sufficient to produce the change. If such a film is allowed to harden for three hours and then treated with silver nitrate, the rings are spiral in form and in groups of three. If a little calcium hypochlorite is added to the gelatin and the film allowed to harden for an hour, narrow rings close together are formed by two precipitations.  
J. F. S.

**Some Problems in Contact Catalysis.** WILDER D. BANCROFT (*Trans. Amer. Electrochem. Soc.*, 1919, **36**, reprint).—A number of specific cases of catalytic reactions are cited where a satisfactory explanation of the mechanism of catalysis is not available, and further study of these is suggested. Thus, the reaction  $\text{COCl}_2 + \text{H}_2\text{O} = \text{CO}_2 + 2\text{HCl}$  is, so far as is known, irreversible. In the presence of excess of water the reaction goes to completion, but in the presence of concentrated hydrochloric acid the rate of hydrolysis is

negligible. A theory is suggested, but study is necessary to prove it. Also, trichloromethyl chloroformate (superpalite) reacts as follows in the presence of alumina:  $\text{CCl}_3\cdot\text{O}\cdot\text{COCl}=\text{CO}_2+\text{CCl}_4$ , and in the presence of ferric oxide,  $\text{CCl}_3\cdot\text{O}\cdot\text{COCl}=2\text{COCl}_2$ . The reverse reaction has never been made to take place to any extent. Yet, when some superpalite and ferric oxide were placed in a tube the reaction soon came to an apparent end. When the temperature was raised a little the reaction went further and did not reverse on cooling. It is suggested that this phenomenon was due to poisoning of the ferric oxide. Finally, some experiments by Lind are cited which may, if desired, be regarded as the displacement of an equilibrium by a catalytic agent. If radium emanation is placed in water in the liquid phase, hydrogen and oxygen are formed and escape into the vapour phase; if the emanation is moved up into the vapour phase oxygen and hydrogen are caused to combine. Additional examples are cited and some interesting lines of experiments suggested.

CHEMICAL ABSTRACTS.

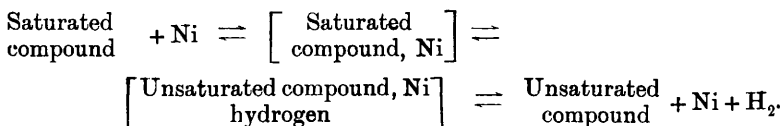
**Catalytic Decomposition of Hydrogen Peroxide.** GÖSTA PHRAGMÉN (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, 5, No. 22, 1—13).—The rate of decomposition of hydrogen peroxide in alkali phosphate or sodium hydroxide solutions has been determined at 17—18°. In the phosphate mixtures, it is shown that the reaction velocity reaches a maximum at  $P_v=11.8$ . In alkaline hydroxide solutions, the velocity is not easily reproducible, and sometimes gives a large value and sometimes a small value. Since the velocity decreases with both increasing and decreasing hydrogen-ion concentration, it is assumed that hydrogen peroxide forms a salt with sodium hydroxide which is very stable, and that only the undissociated hydrogen peroxide molecules undergo decomposition. The decomposition of hydrogen peroxide by yeast extract in the presence of a phosphate buffer mixture has been determined at 17—18°. It is shown that fresh yeast decomposes dilute hydrogen peroxide without sending a soluble enzyme into the surrounding liquid. The reaction is of the first order between certain limits, and the reaction coefficient increases proportionally to the quantity of yeast. The catalytic action per cell or per gram can be increased by treating the yeast with sugar solution before use. The reaction constant is no criterion of the quantity of catalase in the cells.

J. F. S.

**Catalytic Actions at Solid Surfaces. II. Transference of Hydrogen from Saturated to Unsaturated Organic Compounds in the Liquid State in Presence of Metallic Nickel.** E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1919, [A], 96, 322—329. Compare A., 1919, ii, 403).—The evidence that metallic catalysts, during the hydrogenation process, interact primarily with the unsaturated organic compound, together with the resemblance of the whole process to enzyme action (*loc. cit.*), led to the consideration whether the catalytic action, like that

of certain enzymes, might not be reversible. Evidence in support of this view has now been obtained. At 180°, an equimolecular mixture of *cyclohexanol* and methyl cinnamate may, in the presence of nickel, be transformed into one in which about 10% of the cinnamic ester has become hydrogenated to methyl  $\beta$ -phenylpropionate, the *cyclohexanol* being transformed into *cyclohexanone*. The experiments indicate that it is necessary that both components of the system should be present in the liquid state. A similar action took place to a certain extent at 230°, when the *cyclohexanol* was replaced either by dimethyl*cyclohexane* or by dihydropinene. Similarly, a mixture of ethyl stearate and methyl cinnamate when heated at 230° with catalytic nickel gave a product containing small quantities of methyl  $\beta$ -phenylpropionate and ethyl oleate. An important point to note is that simultaneous dehydrogenation and hydrogenation have now been effected at temperatures not far removed from the general optimum hydrogenation range (170—180°), and that hydrogen has been transferred from one compound to another, instead of from one molecule to another of the same species, as was observed by Zelinski and Glinka (compare A., 1911, i, 870).

There is no absolute proof that the mechanism of the change is not dependent on the production of hydrides of nickel, but the authors prefer to regard it as a further case of the catalytic equilibria, previously discussed, which may be indicated as follows:



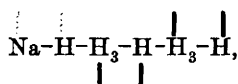
The ultimate equilibrium will depend on the resultant of the varying affinity for nickel of the saturated and unsaturated compounds involved.

This view of catalytic hydrogenation and dehydrogenation affords some explanation of the products obtained (compare Moore, *J. Soc. Chem. Ind.*, 1919, **38**, 320r) during the hydrogenation of unsaturated glycerides, where partial isomerisation occurs. It is suggested that, in the hydrogenation of ethyl oleate, a portion of the freshly produced ethyl stearate in contact with the nickel undergoes dehydrogenation, the hydrogen liberated being transferred to more ethyl oleate, the "dehydrogenated ethyl stearate" formed being the ethyl  $\Delta^1$ -oleate isolated by Moore (*loc. cit.*). W. G.

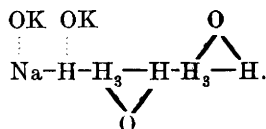
### Constitution and Structure of the Chemical Element.

HAWKSWORTH COLLINS (*Chem. News*, 1919, **119**, 295—296).—Single electropositive charges emanate from masses of 1 (hydrogen), 7 (lithium), 23 (sodium), and 39 (potassium), also two electropositive charges emanate from 4 (helium), of which one has been shown to emanate from a mass 3 ( $\text{H}_3$ ), hence single electropositive charges emanate from masses 1, 3, 7, 23, 39. Taking the first twenty-six elements, it is shown that twenty of these may have their

atomic weights split up into the above-named numbers in such a way that the number of parts is the same as the maximum valency. All the parts are odd numbers, and the non-metallic elements are characterised from the metallic by the presence of one or more portions (1 + 3) (helium). Electropositive forces are distinguished from electronegative forces by the following rule: an electropositive force emanates from each of the masses 1, 3, 7, 23, 39, except when an element has one or more portions (1 + 3), in which cases electropositive forces emanate from these portions, whilst electronegative forces emanate from each of the remaining portions of the element. Hydrogen forms the connecting link in the structure of these elements. From tables given in the paper, it is shown that the longer the chain of  $-H-H_3$ , the more volatile the element and the stronger the electronegative forces from the metallic portions. On this basis, the structure of the sulphur atom is given as



in which Na represents 23, H represents 1, and  $H_3$  3. The thick lines represent electropositive charges, the curly lines electronegative charges, and the thin lines forces which are not chemically evident, but which have to be overcome before the element can be disintegrated. The atomic number of sodium is 11, that of H and  $H_3$  unity, which makes the atomic number of sulphur 16, which is in keeping with fact. The formula therefore shows the connexion between atomic weight, atomic number, and maximum valency, and distinguishes between electropositive and electronegative charges. The molecule  $K_2SO_4$  may therefore be represented:



J. F. S.

**A Model of Radioactive Atoms.** TORAHIKO TERADA (*Proc. Phys. Math. Soc. Japan*, 1919, [3], 1, 185—195).—According to the recent view of atomic structure, an atom consists of a positive nucleus about which a number of electrons are revolving. The conception of the positive nucleus is slightly extended by considering the case of two heavy nuclei with opposite charges revolving about the common centre of mass. Assuming a primary with the larger mass having a positive resultant charge, and the secondary of smaller mass charged negatively as a whole, and leaving out of consideration the ring electrons, it is evident that the two members of the nuclear system will exert on each other a mutual action analogous to the tidal action in the case of the gravitating planetary system. Both members are considered to consist of a number of positive and negative elementary charges, bound together by some unknown forces; also most of the positive charges are assumed to



consist of two elementary charges, as in the case of  $\alpha$ -particles. When the tidal action exceeds a certain limit, the secondary may become unstable, and when the elementary charges in the two substances happen to take a definite configuration, one of the charges may escape and be projected from the nuclear system with the momentum possessed during the orbital motion. If the negative secondary loses a positive charge by the expulsion of an  $\alpha$ -particle, the attraction of the primary will increase, and the orbital velocity be accelerated. In actual radioactive transformations, the velocities of the expulsion of the  $\alpha$ -particles generally increase with successive transformations, although with some exceptions. The tidal action will increase with the decreasing distance between the two nuclei, and consequently the chance of disruption will increase, because the chance of the  $\alpha$ -particle stepping out of the critical threshold will increase. The result will be the shortening of the life of the atom in question. This seems to suggest a possible way of explaining Geiger and Nuttall's law concerning the relation between the average lives of radio-elements belonging to a disintegration series and the velocities of the  $\alpha$ -particles emitted from these elements. If the two members of the nuclear system gradually approach each other by successive emission, a stage may be attained at which the two substances are amalgamated into one, provided the resulting configuration is a stable one. When this final stage is reached, the disintegration will be stopped and the end-product of the radioactive transformation will be reached. One of the simplest systems conceivable is proposed as a provisional working model, and the consequences tested in the light of the available experimental data.

CHEMICAL ABSTRACTS.

**Metals and Non-metals.** A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 119—125).—The author explains the positive charge of the chlorine electrode by assuming that the chlorine atom has the power of splitting off and absorbing electrons, and, further, that these two processes can take place side by side. This is represented by the equations  $XCl_{2g} \rightleftharpoons 2XCl_g' + 2X\ominus_g$  and  $YCl_{2g} + 2Y\ominus_g \rightleftharpoons 2YCl_g'$ , in which  $X$  and  $Y$  indicate the fractions of the chlorine molecules which have undergone positive and negative ionisation respectively. As the electrons which are absorbed in the second action proceed from the first, it is clear that  $Y \leq X$ , but, chlorine being a non-metal, both fractions must be extremely small. If, then, it is further assumed that the negative ions almost exclusively pass into solution, the electrode will then possess a positive charge. Extending the above hypothesis, the author shows that there is only a difference of degree between metals and non-metals, and not one of kind. If it be assumed that all elements can both split off and absorb electrons, then the factor  $X$  is comparatively large for metals and small for non-metals, and for non-metals  $Y$  is exceedingly small. This view is in keeping with the large electric conductivity of metals and the small conductivity of non-metals. In the case of the metals, the

positive ions have the greater solubility, and the negative ions in the case of the non-metals. This is in keeping with the different electromotive behaviour of metals and non-metals. The difference in solubility between the two ions is so great as to justify the assumption that only one kind is present in solution. Amphoteric elements probably send appreciable quantities of both positive and negative ions into solution.

J. F. S.

**Atomic Structure and the Periodic Law.** TYCHO E:SON AURÉN (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, 5, No. 18, 1—7).—A theoretical paper. The author's experiments on the absorption of Röntgen rays (details not yet published) indicate the possibility of differentiating between the inner and outer electrons in the atom, the outer electrons being identical with the so-called valency electrons and playing a totally different rôle from the inner electrons. In accordance with this view, Kossel's table (A., 1916, ii, 243) for the first twenty-three elements of the periodic system is modified. The number of electrons in the outer ring increases from one in the case of hydrogen to seven in the case of nitrogen; it does not become eight in the case of oxygen, but four electrons go from the outer ring to the inner system; the number of outer electrons then increases to seven again for sodium, whilst for magnesium four more electrons go from the outer to the inner system, and so on. The consequences of these conceptions are discussed, special reference being made to the valencies of the elements in the various groups. For example, it is argued that sulphur should be bivalent; the existence of  $\text{SO}_3$  and  $\text{SF}_6$  is no definite proof of the sexavalency of sulphur, since the former can be represented by a ring structure and the latter as  $\text{F} \begin{array}{c} \text{F} \\ \text{F} \end{array} > \text{F} \cdot \text{S} \cdot \text{F} < \begin{array}{c} \text{F} \\ \text{F} \end{array}$ .

T. S. P.

**Atomic Numbers.** HAWKSWORTH COLLINS (*Chem. News*, 1919, 119, 285—287).—The author considers the atomic weights (nearest whole number), atomic numbers, and valencies of the first twenty-eight elements, taken in order of their atomic weights. It is shown that, with four exceptions (glucinum, nitrogen, scandium, and cobalt), when the atomic weight is represented by an even number, the maximum valency and the atomic number are both represented by even numbers, and when the atomic weight is represented by an odd number, the valency and the atomic number are also represented by odd numbers. Further, the elements, with the exceptions named, follow one another alternately odd and even. The probability that this condition of things has happened accidentally is  $1:4^{28}$ . The reason for the odd and even rule is shown to be as follows. If the atomic weight of an element be split up into 3's and 1's alternately, always commencing with a 3, the number of portions obtained gives the atomic number, and should the atomic number be an even number, the atomic weight must of necessity be an even number, but if the atomic number is odd, the atomic weight must also be odd. The atomic number is exactly

obtained as follows. If the atomic weight is an even number, the atomic number is one-half of the atomic weight, but if the atomic weight is an odd number, the atomic number is one-half of the atomic weight from which 1 has been subtracted. J. F. S.

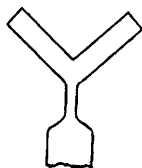
**The Mathematical Possibility of Increasing the Yield or of Reducing the Proportion of the Reacting Substances in certain Chemical Reactions.** ANGEL PÉREZ HERNÁNDEZ (*Anal. Fis. Quim.*, 1918, **16**, 302—317).—An elementary mathematical method is illustrated for the construction of chemical equations in which two or more reactions are simultaneously involved.

W. S. M.

**Some Biographical Notes on Hermannus Follinus.** W. P. JORISSEN (*Chem. Weekblad*, 1919, **16**, 947—951).—The biographer gives a very brief sketch of Hermannus Follinus, who was born in Friesland, *circa* 1590, and joined the medical faculty in Cologne, where he died of the plague in 1622. He was the author of "Den Nederlandsche Sleutel van't Secreet der Philosophie" (Key to the Secrets of Philosophy), "Physiognomie," and "Simonides, ofte die Memori-const" (Science of Memory).

W. J. W.

**An Apparatus for Preparing in a Very Short Time Homogeneous Liquid Mixtures.** PIERRE JOLIBOIS (*Compt. rend.*, 1919, **169**, 1095—1098).—A simple apparatus is described consist-



ing essentially of two containers, one for each of the liquids to be mixed, arranged so as to deliver into the two limbs of a Y-tube of the pattern shown the liquids in the requisite proportion. The diameter of the Y-tube is 6.2 mm., and the lower limb has a restriction as shown 1.5 mm. in diameter and 2 cm. long. With such an apparatus a homogeneous mixture may be obtained from two miscible liquids in 1/100th of a second.

W. G.

**Eykman's Suction Pump.** L. TH. REICHER (*Chem. Weekblad.*, 1919, **16**, 951—956).—This apparatus embodies the principle of Geissler's suction pump, but the operation of filling the vessel in communication with the apparatus which has to be exhausted, by lifting a second vessel periodically, is avoided. Special features of Eykman's pump are a "vacuum reservoir," containing air-free, concentrated sulphuric acid, and a drying device also filled with that liquid. A sketch of the complete apparatus is given and its mode of operation described.

W. J. W.

## Inorganic Chemistry.

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**Model of a Triatomic Hydrogen Molecule.** N. BOHR (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, 5, No. 28, 1—16).—A theoretical paper in which it is shown that triatomic hydrogen consists of three nuclei and three electrons. The electrons rotate at equal angular intervals in a common circular orbit, whilst the three nuclei are placed on the axis of this orbit. It is shown that  $H_3$  cannot be formed from  $H_2$  molecules without the supply of energy from external sources. On the other hand, it is shown that in hydrogen gas which is ionised by external agencies, molecules of  $H_3$  may be formed by successive processes, each of which is accompanied by the production of heat. J. F. S.

**The Solubility of Sulphur Dioxide in Sulphuric Acid.** FRANK DOUGLAS MILES and JOSEPH FENTON (*T.*, 1920, 117, 59—61).

**Some Points of View concerning the Nitrogen Question and Related Problems.** L. HAMBURGER (*Chem. Weekblad*, 1919, 16, 560—595).—An amplified version of a lecture delivered before the Algemeen Bestuur der Nederlandsche Chemische Vereeniging on July 13th, 1918. W. S. M.

**Electrochemical Reactions of Nitrogen and the accompanying Spectroscopic Phenomena.** L. HAMBURGER (*Chem. Weekblad*, 1918, 15, 931—942).—A mixture of nitrogen and hydrogen in stoichiometrical proportions under a pressure of 12 mm. of mercury was passed through a quartz capillary tube and subjected to a direct-current discharge of 12 amperes per square cm. A yield of 109 mg. of ammonia per kilowatt-hour was obtained. Reduction of the current density and simultaneous increase of the time of exposure to the discharge gave much smaller yields. The conditions for a high yield of ammonia thus correspond with those necessary for the formation of activated atomic nitrogen and hydrogen. The discharge through mixtures of nitrogen with hydrogen, oxygen, and carbon monoxide was examined spectroscopically. In every case evidence of the disruption of the molecules and formation of new compounds, such as cyanogen, was obtained. W. S. M.

**The Dissociation Constant of Nitrogen Peroxide.** EUGÈNE WOURTZEL (*Compt. rend.*, 1919, 169, 1397—1400).—As a result of measurements at temperatures between  $0^\circ$  and  $86.5^\circ$  it is shown that the variation of the dissociation constant with the temperature is given by  $\log K/T = 8.9908 - 2810.5/T$ , and calculated from this the heat of polymerisation is 12,850 cal., exact to 0.5%. W. G.

**Luminescence and Ionisation in the Oxidation of Phosphorous Oxide.** HERMAN RINDE (*Arkiv Kem. Min. Geol.*, 1917—18, 7, No. 7, 1—21).—A mixture of oxygen and carbon

dioxide, dried by means of sulphuric acid, calcium chloride, and phosphoric oxide, and warmed to a suitable temperature, is passed through two absorption bulbs containing phosphorous oxide, with the vapour of which it becomes saturated. No luminescence takes place with the dried gas, but when the mixture is led over the surface of water contained in a test-tube, luminescence appears. The absorption bulbs and test-tube containing water were immersed in a thermostat at constant temperature, and the total intensity of the luminescence was measured photographically by means of a Martens' photometer.

There is no luminescence in pure carbon dioxide, but the addition of oxygen causes the phenomenon to appear, and its intensity is greatest in mixtures containing 5% of oxygen. With increase in the percentage of oxygen the intensity decreases and attains an approximately constant value between 50% and 100% oxygen (compare Scharff, A., 1908, ii, 373). When a tube, 3.75 metres long, is inserted between the absorption bulbs and the test-tube, the intensity of the luminescence is about the same for mixtures containing a low percentage (about 5%) of oxygen, but it rapidly diminishes with increasing oxygen content to a lower value than before the tube was inserted. At the same time the tube becomes covered with a deposit of phosphoric oxide. These results indicate that the phosphorous oxide is oxidised without luminescence by the dry oxygen, and that the diminished luminescence with mixtures containing high percentages of oxygen is due to the fact that the gas coming into contact with the water-vapour contains much less phosphorous oxide.

According to Scharff (*loc. cit.*), the merest trace of water-vapour is sufficient to cause luminescence, but the author finds that when the vapour pressure of the water-vapour is diminished, as, for example, by using concentrated sulphuric acid instead of water, the luminescence becomes very feeble.

As with all gas reactions, the width of the test-tube containing the water affects the intensity of the luminescence. The wider the test-tube the less the luminescence.

The author suggests that in dry oxygen phosphorous oxide is directly oxidised to phosphoric oxide, but that in moist oxygen an intermediate compound, X, is formed, according to the equation  $P_4O_6 + H_2O + O_2 \rightarrow X \rightarrow H_3PO_4$ .

Ionisation does not occur in a gas free from oxygen, but containing phosphorous oxide. In the presence of oxygen ionisation takes place, and the author has measured the saturation current (compare Harms, A., 1904, ii, 331; Bloch, A., 1905, ii, 72). The ionisation is not a photoelectric effect, as shown by measurement of the saturation current with different electrodes, but is caused by the oxidation of an unknown intermediate product formed from phosphorous oxide and water vapour. The mobility of the ions is small compared with that of ordinary gaseous ions, but of the same order as that obtained for the ions formed in the oxidation of phosphorus (compare Harms and Bloch, *loc. cit.*), and it is very probable that the ions are produced by the same reaction in both cases. T. S. P.

**Some Chemical Characters of Ancient Charcoals.** T. C. CANTRILL (*Archaeol. Cambrensis*, 1919, 365—392).—Although the pieces of charcoal or charred wood found during archæological excavations are more readily attacked or dissolved by such reagents as nitric acid and potassium chlorate, and hypochlorite solution, thus differing from modern, well-burnt charcoal, the author considers that the solubility, etc., of some of the ancient charcoals is simply due to their incomplete carbonisation, and that there is doubt that they were produced by the agency of fire. The situations in which certain of the charcoals are found negatives the opinion that the blackening of wood was due to the action of peaty soil. W. P. S.

**Artificial Production of Diamond.** SIR CHARLES ALGERNON PARSONS (*Phil. Trans.*, 1919, A, 220, 67—107).—Bakerian lecture. It is shown from experiments that all the hydrocarbons, chlorides of carbon, and oxides of carbon deposit amorphous carbon or graphite on a carbon rod electrically heated at any pressure up to 4400 atms. and in a few cases up to 6000 atms. At 15,000 atms. carbon and graphite electrically heated are either transformed into soft graphite or are first vaporised and condensed as such. The experiment of compressing a mixture of acetylene and oxygen and the production of a temperature in excess of that required to vaporise carbon, accompanied by a momentary pressure of 15,000 atms., shows that the failure to convert graphite into diamond is not due to lack of temperature. The experiment of firing a high-velocity steel bullet with cupped nose through vaporising carbon into a hole in a block of steel raises the pressure momentarily to 300,000 atms. and the temperature probably 1000°, but the fact that only a few minute crystals resembling diamond were produced (probably from the iron) leaves a doubt as to whether the duration of the pressure was sufficient to start a recognisable transformation of graphite to diamond. A repetition of many of the experiments, in which diamond has been claimed to be formed, has given negative results except where iron has played a part. A list of the experiments tried together with conditions and results is given in an appendix to the paper. In repeating Moissan's experiments it is shown that when a crucible of molten iron is subjected to pressure more than three times as great as can be produced by these contractile forces, the yield of diamond is not increased; on the other hand, if the occluded gases are imprisoned, then the yield of diamond is about the same as when the crucible is plunged into water, whilst if the conditions are such as to allow a free passage of the gases through the skin of the ingot the yield is at once reduced, even though the bulk pressure on the ingot is the same. Experiments in vacuum, from 75 mm. to X-ray vacuum, show generally that as the pressure is decreased the yield of diamond is diminished, and below 2 mm. no diamond could be detected. The greatest percentage of diamond occurred when the atmosphere round the crucible consisted of 95% carbon monoxide, 1% hydrogen, 2% hydrocarbons, 2% nitrogen. The weight of diamond is about 1/20,000 of the weight of the iron. It appears that the formation of diamond in rapidly cooling iron takes

place when it is solid or in a plastic condition or even at a lower temperature. The rapid pitting of a diamond in highly carburised iron just above its melting point is so pronounced that the largest diamond hitherto produced artificially would be destroyed in a few seconds if the iron matrix were molten. The experiments indicate that the bulk pressure on the metal does not play a part in the formation of diamonds, but that the previous heat treatment, the impurities in the iron, and the condition of the gases within the metal are the important factors. The iron in the most successful experiment has a concentration of diamond 270 times as great as the blue ground in the South African mines. J. F. S.

### **Production of Carbon Monoxide in the Flames of Gases.**

ANDRÉ KLING and DANIEL FLORENTIN (*Compt. rend.*, 1919, **169**, 1404—1406).—A number of gases, the carbon monoxide content of which varied from 0% to 60%, were burnt at differing types of burners in a large chamber, and the carbon monoxide in the air was estimated at the end of one hour. The results indicate that the production of carbon monoxide is due principally to the sudden cooling of the flame. For a given type of burner the amount of carbon monoxide present in the gas to be burnt is without influence on the amount present in the products of combustion. The Auer burner produced comparatively large amounts of carbon monoxide, this production being due apparently to the presence of the incandescent mantle. The hourly production of carbon monoxide with certain common types of burners is sufficiently high to warrant further efforts to improve them. W. G.

### **Atomic Structure of Metals in Solid Solution.**

A. L. FEILD (*Chem. and Met. Eng.*, 1919, **21**, 566—570).—The reason for the difference in physical properties of solid solution alloys and their components has been investigated. It is concluded that the alloys retain in the solid state the same atomic structure as in the liquid state, the metals being in the amorphous form. Such a solid solution is analogous to a supercooled liquid with the same electrical resistance and temperature-coefficient of resistance as in the molten state. Experiments with alloys of nickel and chromium, and of gold and silver, confirm this theory. It does not apply to eutectic alloys. The hardness of alloys is also ascribed to an amorphous state.

W. J. W.

### **Transition of Dry Ammonium Chloride.**

ALEXANDER SMITH, HERBERT EASTLACK, and GEORGE SCATCHARD (*J. Amer. Chem. Soc.*, 1919, **41**, 1961—1969).—Time-temperature curves, both heating and cooling, have been made for absolutely dry ammonium chloride with the object of ascertaining whether the dry material changes into a second crystalline form at 184.5°, as does the undried material. It is shown that ammonium chloride which has been dried for forty-five days at 155—165°, or for three years with phosphoric oxide in a high vacuum, undergoes exactly the same transition at 184.5° as the undried salt. In the thermal measure-

ment of transition points in a high vacuum confusion may result from the greater thermal effects of distillation. Wegscheider's explanations of the anomalous vapour density of dried ammonium chloride by a failure to undergo transition in the absence of water are untenable in the light of these results (A., 1918, ii, 298).

J. F. S.

**Lithium Silicate.** K. ALB. VESTERBERG (*Medd. K. Vetenskapskad. Nobel-Inst.*, 1919, 5, No. 30, 1—9).—Amorphous silicic acid, which has been dried at  $100^{\circ}$ , dissolves slowly in a fairly concentrated (approx. 2*N*) solution of lithium hydroxide at the ordinary temperature, giving finally a solution containing 3.4 mols. of  $\text{SiO}_2$  to 1 mol. of  $\text{Li}_2\text{O}$ . Thus lithium behaves similarly to potassium and sodium in giving soluble silicates containing a large excess of acid over the base (compare A., 1915, ii, 344; also Jordis and Kanter, A., 1903, ii, 475, 542, 595; Jordis, 1908, ii, 291; Ordway, 1908, ii, 37). In warm lithium hydroxide solution, however, silicic acid is almost insoluble, the acid being transformed into a practically insoluble lithium silicate.

*Lithium metasilicate* occurs in two modifications, the one easily soluble and the other almost insoluble. The latter, which has the formula  $\text{Li}_2\text{SiO}_3 \cdot \text{H}_2\text{O}$ , is obtained as a white, granular precipitate when a fairly concentrated solution of sodium metasilicate is mixed with the equivalent quantity of lithium chloride, lithium hydroxide added in approximately normal concentration, and the solution heated for a short time at  $80$ — $90^{\circ}$ . It can also be obtained by dissolving silicic acid, which has been dried at a temperature not higher than  $100^{\circ}$ , in twice the theoretical amount of 2*N*-lithium hydroxide solution at the ordinary temperature, and then heating the solution for a short time at  $80^{\circ}$ .

T. S. P.

**A New Physicochemical Method of Analysis of Precipitates. Application to the Study of the Calcium Phosphates.**

PIERRE JOLIBOIS (*Compt. rend.*, 1919, 169, 1161—1163).—The two solutions, from which the precipitate is obtained, are very rapidly mixed by means of the apparatus previously described (this vol., ii, 107), and the precipitate is collected and analysed and the supernatant liquid is also analysed when equilibrium has been reached. Applying this method to the study of mixtures of solutions of calcium hydroxide and phosphoric acid in varying proportions, the author has prepared and characterised a new calcium phosphate having the composition  $2\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$ . This phosphate occurs in a crystalline form, and in the presence of excess of phosphoric acid is slowly converted into the dicalcium phosphate.

W. G.

**Research on Magnesia Alba by Joseph Black, Petrus Driessen and Others.**

W. P. JORISSEN (*Chem. Weekblad*, 1919, 16, 1579—1589).—The author gives a retrospect of the researches of Joseph Black on magnesia alba, which led to his discovery of carbon dioxide ("fixed air"). The methods of preparation of



magnesia alba, described in the literature on the subject, are variations of the original experiments of Black, Driessen, and other investigators of the eighteenth century. W. J. W.

**Zincates of Sodium. Equilibria in the System  $\text{Na}_2\text{O}-\text{ZnO}-\text{H}_2\text{O}$ .** F. GOUDRIAAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 179—189).—The solubility isotherm in the system  $\text{Na}_2\text{O}-\text{ZnO}-\text{H}_2\text{O}$  has been completely determined at  $30^\circ$  by dissolving zinc oxide in solutions of sodium hydroxide of various concentrations and determining the solubility. The following substances appear as stable, solid phases: zinc oxide, sodium zincate,  $\text{Na}_2\text{O}, \text{ZnO}, 4\text{H}_2\text{O}$ , and the monohydrate of sodium hydroxide. Sodium zincate forms very strongly incongruent solutions; in solutions containing 1 part of sodium hydroxide to 2 parts of water, it is decomposed, with separation of zinc oxide. Amorphous, gelatinous zinc hydroxide is to be regarded as a phase of a varying water content; it is impossible to remove all adsorbed ions from it, and it is metastable as regards zinc hydroxide. In special circumstances zinc hydroxide may be obtained as a crystalline phase of the constant composition,  $\text{Zn}(\text{OH})_2$ . This crystallised hydroxide is metastable at  $30^\circ$  with respect of zinc oxide. J. F. S.

**Reguline Lead Peroxide.** WILH. PALMAER (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 31, 1—15).—Compact lead dioxide has been prepared by the electrolysis of lead nitrate solution. The product is greyish-black in colour and has a pronounced crystalline appearance, and contains no impurities; it has a hardness 5—6 and D 9.360. In all respects it is similar to the mineral plattnerite. The specific resistance at  $18^\circ$  is 0.000845 ohm and the specific conductivity 1180 ohm<sup>-1</sup>. The temperature-coefficient of the conductivity is 1/8% per degree. J. F. S.

**Aluminium Spontaneously Oxidisable in the Air.** E. KOHN-ABREST (*Compt. rend.*, 1919, **169**, 1393—1395).—Attention is drawn to the fact that when aluminium is distilled in a vacuum at  $1100^\circ$ , the globules of aluminium remaining undistilled at the end of sixteen to twenty hours, when exposed to the air at the ordinary temperature, undergo spontaneous oxidation, giving a yellowish-grey powder, which is a mixture of the oxide and the finely divided metal. This aluminium only contained 0.4% of iron and 0.5% of silicon. W. G.

**Chemical Method for the Determination of the Strength of Sparingly Soluble Inorganic Bases.** K. A. VESTERBERG (*Arkiv. Kem. Min. Geol.*, 1917, **6**, No. 11, 1—20).—The determination of the hydrolysis of salts of sparingly soluble inorganic bases by electrometric methods and methods depending on the inversion of sucrose or the hydrolysis of esters has given very varying results, according to the methods used (compare Denham, T., 1908, **93**, 41; Lundén, A., 1908, ii, 164). Farmer's method (T.,

1901, 79, 863) for the determination of hydrolysis does not give correct values, owing to the disturbance of the hydrolytic equilibrium by the partial extraction of the one product of hydrolysis. In the case of cobalt acetate, for example, too little acetic acid is extracted. The author makes use of Farmer's method, but modifies and corrects it as follows. The solution is extracted with twice its volume of ether; the same ethereal solution is again used to extract half its volume of a fresh solution of cobalt acetate. This process is repeated until the concentration of the ether phase becomes constant with respect to acetic acid, showing that it is in equilibrium with hydrolysed cobalt acetate solution, in which base and acid are present in equivalent proportions. The percentage hydrolysis can then be readily calculated. Usually, the concentration of the ether phase becomes constant after three extractions.

Corrections have to be made for the increase in volume of the aqueous phase by solution of ether, and the ether and salts used have to be specially purified. If the acetate is difficult to obtain pure, accurate results can be obtained by using a solution of the sulphate or nitrate to which an equivalent quantity of sodium acetate has been added.

The determinations were carried out at  $18^{\circ}$ , the distribution coefficient of acetic acid between ether and water being taken as 2.1. The results obtained for percentage hydrolysis were as follows:  $N/2$ -cobalt acetate, 0.19;  $N/5$ , 0.165;  $N/2$ -nickel acetate, 0.435;  $N/5$ , 0.38. It follows that cobalt hydroxide is a stronger base than nickel hydroxide, and this agrees with the stabilities of their sulphates. The fact that the hydrolysis is greater in the stronger solutions may be due to the greater salting-out effect of the acetate on the acetic acid.

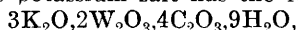
The hydrolysis of lanthanum acetate in  $N/5$ -solution was 0.315% and in  $N/10$ -solution 0.286%, the value 0.31% being taken as correct for both solutions, the differences being within the error of experiment. Lanthanum acetate was found to have  $1\frac{1}{2}\text{H}_2\text{O}$  of crystallisation, the solubility at  $18^{\circ}$  being 20.43 grams of the anhydrous salt in 100 grams of water; it loses  $\frac{1}{2}\text{H}_2\text{O}$  at  $100^{\circ}$ . T. S. P.

**A New Complex Form of Chromic Sulphate.** A. RECOURA (*Compt. rend.*, 1919, 169, 1163—1166).—When a  $N/2$ -solution of chromic sulphate is allowed to remain until equilibrium is reached, in so far as the formation of the green sulphate is concerned, and then evaporated to saturation point in a vacuum, on the addition of an excess of alcohol a lilac-grey precipitate is formed. If this precipitate is immediately collected and washed with a little ether, it is found to contain  $18\text{H}_2\text{O}$  and to have the whole of its  $\text{SO}_4$  precipitable by barium chloride. It changes, however, spontaneously and rapidly when exposed to the air, and at the end of the day contains only  $16\text{H}_2\text{O}$ , and gives no precipitate with barium chloride. If left in a desiccator, its water content finally drops to  $12\text{H}_2\text{O}$ . The constitution of this new complex sulphate has not yet been determined. W. G.

**Method of Obtaining, and Optical Study of, Crystals of Sodium Chromate Tetrahydrate.** LUCIEN DELHAYE (*Bull. Soc. franç. min.*, 1918, **41**, 80—92).—Deliquescent monoclinic crystals 5 mm. in length can be obtained by allowing a solution of sodium chromate saturated at 50° to cool to about 27°, filtering, and keeping for several days with occasional shaking. The refractive indices, optic axial angle, dispersion, etc., have been measured for light of various wave-lengths.

CHEMICAL ABSTRACTS.

**Chemistry of Quinquevalent Tungsten.** OSCAR O:SON COLLENBERG (*Arkiv. Kem. Min. Geol.*, 1918, **7**, No. 5, 1—35).—Solutions of tungstic acid and alkali tungstates in oxalic acid or alkali oxalate solutions are readily reduced to quinquevalent tungsten derivatives. From the solution of tungstic acid in oxalic acid, pure, solid reduction products could not be isolated, but if the solution is saturated with hydrogen chloride and then treated with a solution of rubidium chloride in concentrated hydrochloric acid, the compound *dirubidium pentachlorotungstite*,  $\text{Rb}_2\text{WOCl}_5$ , crystallises out in very good yield. When a solution of an alkali tungstate in oxalic acid solution containing a slight excess of alkali oxalate is reduced with tin foil, the colour passes through dark blue and becomes green, yellowish-green, and finally red. On cooling the highly concentrated solution, oxalic acid, alkali oxalate, and tin oxalate separate. The tin is removed by hydrogen sulphide from the solution, and, on adding alcohol, a dark reddish-brown powder separates. On dissolving the powder in water and adding an excess of alkali iodide or bromide, it is obtained pure. In this way, the *oxalo-tungstites of sodium, potassium, and ammonium* have been prepared. The potassium salt has the formula



whilst the sodium salt is similar, except that it contains  $12\text{H}_2\text{O}$ . The oxalo-tungstites are suitable substances for the preparation of other quinquevalent tungsten derivatives. They dissolve readily in hydrochloric acid to produce deep blue solutions, from which the oxy-chlorides of quinquevalent tungsten may be separated. They are soluble in potassium thiocyanate solution, producing deep red-coloured solutions; they dissolve in concentrated hydrofluoric acid solution, producing violet solutions. On boiling with potassium cyanide, yellow solutions are obtained, from which double cyanides of the type  $\text{M}_4\text{W}(\text{CN})_8$  may be isolated. The alkali oxalo-tungstites may be converted into chloro-tungstites by the following methods: (a) by treating the hydrochloric acid solution of an alkali (K or  $\text{NH}_4$ ) oxalo-tungstite with hydrogen chloride, (b) by adding chlorides (rubidium, caesium, aniline, tetraethylammonium, and tetrapropylammonium) to the hydrochloric acid solution of an oxalo-tungstite, and (c) by adding either pyridinium chloride or quinolinium chloride to a solution of ammonium chloro-tungstite in concentrated hydrochloric acid. By these methods, derivatives of the types: (i)  $\text{M}_2\text{WOCl}_5 (\text{M} = \text{NH}_4, \text{Rb}, \text{Cs}, \text{C}_6\text{H}_5\cdot\text{NH}_3)$ ,  
(ii)  $\text{M}_2\text{WOCl}_5 \cdot x\text{H}_2\text{O} (\text{M} = \text{K})$ ,

(iii)  $\text{MWOCl}_4$  ( $\text{M} = \text{C}_5\text{H}_5\text{NH}$ ,  $\text{C}_9\text{H}_7\text{NH}$ ), and (iv)  $\text{MWOCl}_4 \cdot \text{H}_2\text{O}$  ( $\text{M} = [\text{C}_2\text{H}_5]_4\text{N}$ ,  $[\text{C}_3\text{H}_7]_4\text{N}$ ), have been prepared. All the derivatives obtained have been shown by titration with potassium permanganate or by titration with iodine and arsenious acid to contain the tungsten in the quinquivalent condition. The *chloro-tungstites* are finely crystalline powders; they are quite stable in dry air, but at  $60\text{--}70^\circ$  are oxidised, turning blue, and eventually quite white. They are hydrolysed by water, and a reddish-brown hydroxide is produced. In the case of the less soluble compounds, for example, the caesium salt,  $\text{Cs}_2\text{WOCl}_5$ , the hydrolysis is not complete. The chloro-tungstites are soluble in concentrated hydrochloric acid, and in the case of the metal derivatives the solubility decreases with increasing atomic weight; they are insoluble in most organic solvents, except in the case of the rubidium and caesium derivatives, which are soluble in absolute methyl and ethyl alcohol. The solubility in methyl alcohol is very much greater than in ethyl alcohol. Oxidising agents convert the chloro-tungstites into sexavalent tungsten derivatives. A vigorous reaction takes place on treatment with potassium cyanide, with the production of double cyanides of the type  $\text{M}_4\text{W}(\text{CN})_8$ . The compounds of the type (iii) and (iv) are regarded as derivatives of metatungstous acid,  $\text{O}_2\text{W} \cdot \text{OH} \rightarrow \text{Cl}_4\text{W} \cdot \text{OH}$ , whilst those of types (i) and (ii) are regarded as derivatives of orthotungstous acid,  $\text{W}(\text{OH})_5 \rightarrow (\text{HO})_2\text{W}(\text{OH})_3 \rightarrow \text{HCl}_2\text{W} > \text{WCl}_3$ . For the special description and preparation of the individual chloro-tungstites, the original should be consulted.

J. F. S.

**Decomposition of Stannous Chloride by Water and by Potassium Hydroxide Solutions.** C. M. CARSON (*J. Amer. Chem. Soc.*, 1919, **41**, 1969—1977).—Making use of the principles of the phase rule, the author has investigated the action of water and potassium hydroxide on stannous chloride. The experimental results show that the compound,  $2\text{SnCl}_2 \cdot 7\text{Sn}(\text{OH})_2$ , is the most basic of all the basic stannous chlorides. A slightly variable, crystalline material of approximately the formula  $3\text{SnCl}_2 \cdot 5\text{SnO} \cdot 3\text{H}_2\text{O}$  is the precipitate commonly formed by the action of boiling potassium hydroxide on an excess of stannous chloride, and there is no compound of intermediate composition. Whether any basic compound lies between  $3\text{SnCl}_2 \cdot 5\text{SnO} \cdot 3\text{H}_2\text{O}$  and the normal salt was not determined. The precipitates usually formed by the action of water on stannous chloride contain such a large proportion of stannic compound that the analyses are of no value in ascertaining the composition of the basic stannous chlorides.

J. F. S.

**The Peroxides of Bismuth.** RICHARD ROBERT LE GEYT WORSLEY and PHILIP WILFRED ROBERTSON (*T.*, 1920, **117**, 63—67).

**Behaviour of Hydrogen towards Rhodium.** A. GUTBIER and O. MAISCH (*Ber.*, 1919, **52**, [B], 2275—2280).—The experi-

ments were performed in the same manner as with palladium, iridium, and platinum (A., 1913, ii, 608; 1919, ii, 367, 368). The results may be summarised in the following manner. The deep black modification, rhodium-black, is able to absorb far more hydrogen than any other form. The maxima of hydrogen absorption amounted to 180 volumes at  $190^{\circ}$  for the greyish-black form, 165 volumes at  $40^{\circ}$  for the slightly greyish-black variety, and 206 volumes at  $0^{\circ}$  for the deep black modification. (The varieties are obtained in the order given by the reduction of sodium rhodium chloride by hydrazine in faintly acid, neutral and ammoniacal solution respectively; the purest preparations, dried in a vacuum over phosphoric oxide, contained about 3% of water and 0.3% of oxygen.) The absorption of hydrogen by rhodium is much less than by palladium, and corresponds with that observed with platinum. Spongy rhodium, like spongy platinum, only absorbs small amounts of hydrogen.

H. W.

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## Mineralogical Chemistry.

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**Hausmannite in the Batesville District, Arkansas.** H. D. MISER and J. G. FAIRCHILD (*J. Washington Acad. Sci.*, 1920, 10, 1—8).—The abundant manganese ores of this district consist of the oxides psilomelane, hausmannite, braunite, manganite, pyrolusite, and wad, the first two, which occur intimately intergrown, being the commonest. They occur as irregular masses, weighing from less than a pound to 22 tons, embedded in clay, limestone, shale, sandstone, etc. The hausmannite, however, occurs as a replacement material only in the limestone, and as a residual material in clay derived from limestone. Analysis I is of a sample from the W. T. Gray mine near Pfeiffer, and II from Club House mine, near Cushman; they correspond with hausmannite ( $Mn_3O_4$ ) with 13% and 31% admixed psilomelane respectively.

	MnO.	O.	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	SiO <sub>2</sub> .	CaO.
I. ....	91.38	7.78	Nil.	Nil.	Nil.	Trace
II. ....	90.40	8.87	0.48*		0.10	Trace
	MgO.	BaO.	H <sub>2</sub> O.	Total.	Sp. gr.	
I. ....	Trace	0.26	0.62	100.04	4.836	
II. ....	Trace	Nil.	1.03	100.88	4.778	

\* Fe<sub>2</sub>O<sub>3</sub> trace.

The 'braunite' described by Penrose in 1891 is shown to be such a mixture of hausmannite and psilomelane. Braunite is readily distinguished by the fact that it yields considerable gelatinous silica.

L. J. S.

**Analyses of Dolomites.** ALBERT ROTHROCK and J. B. SHUMAKER (*Chem. News*, 1920, **120**, 29—31).—The following analyses of dolomite rocks and dolomitic limestones from various localities show considerable variations from typical dolomite,  $\text{CaMg}(\text{CO}_3)_2$ , which contains  $\text{CaCO}_3$  54·35%,  $\text{MgCO}_3$  45·65%. I, white, compact, crystalline, from Ossining, New York. II, dark grey, massive, from Cumberland. III, light-coloured, massive, from Cerro Gordo, Inyo Co., California. IV, grey, compact with conchoidal fracture, from Frankenstein, Silesia; this approaches magnesite. V, white, compact, and crystalline, resembling marble, from near Keeler, California. VI, greyish-white, crumbly, and saccharoidal, from the Binnenthal, Switzerland. VII, hard, compact, from Gerolstein, Rhine. VIII, light colour with pearly lustre, from Costa da Val, Tyrol;  $2\text{CaCO}_3, \text{MgCO}_3, \text{FeCO}_3$ . IX, greyish-white, compact, from New Almadin, California. X, light grey, granular, and porous, from Raible, Carinthia. XI, grey, large crystals, from Brewster's, New York. XII, *a*, outer layer of pale pink crystals, *b*, inner portion of dark grey crystals. XIII, grey from 'The Dolomites,' Tyrol. XIV, from the Brenner Pass.

	$\text{CaCO}_3$ .	$\text{MgCO}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{Al}_2\text{O}_3$ .	$\text{SiO}_2$ .	Total.	Sp. gr.
I. ....	51·97	37·40	0·20	Trace	10·61	100·18	2·93
II. ....	57·59	24·98	16·05	0·87	0·56	100·05	2·88
III. ....	87·88	11·85	0·09	—	0·06	99·88	2·57
IV. ....	27·04	67·91	3·71	0·73	0·13	99·52	2·9
V. ....	66·08	1·15	0·06	—	32·57	99·86	2·7
VI. ....	49·00	40·23	0·48	—	10·84	100·55	2·85
VII. ....	52·93	44·33	0·80	0·22	1·23	99·51	2·82
VIII. ....	49·59	24·50	2·36	—	0·12	100·01*	3·01
IX. ....	53·28	45·18	8·57	—	0·4	100·11 ?	2·8
X. ....	54·64	45·18	Trace	0·28	0·23	100·33	2·7
XI. ....	59·98	36·83	2·44	—	0·33	99·58	2·9
XIIa. ....	56·63	41·37	1·18	0·63	0·23	100·04	—
XIIb. ....	57·18	36·83	0·89	1·16	3·96	100·02	—
XIII. ....	94·21	4·15	0·56	0·57	0·48	99·97	2·73
XIV. ....	96·25	2·98	0·50		0·35	100·08	—

\* Including  $\text{FeCO}_3$ , 23·44.

L. J. S.

### Analytical Chemistry.

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**Application of the Interferometer to Gas Analysis.** J. D. EDWARDS (*Chem. and Met. Eng.*, 1919, **21**, 560—565).—The gas interferometer measures the difference in refractivity of two gases of binary mixtures. Usually, one of the components is taken as the standard gas, and the difference in refractivity of the mixture and one of its components is determined. For a change of  $a\%$  of one of the components the change in refractivity

$$\Delta R = 273/T \cdot p/760 \cdot a/100(R_1 - R_2).$$



Each scale division corresponds with a definite value of  $\Delta r$ , which is the difference in refraction of the two gases. The calibration of the instrument is described (see also A., 1918, ii, 47). In measuring a small percentage of a gas which deviates appreciably from Boyle's law, a correction is necessitated, as the refractivity of the gas at a low partial pressure differs from the value calculated from the pressure ratios.

In taking readings, calibration curves should be drawn for different temperature and pressure intervals from which readings may be taken by interpolation. A variation of  $3^{\circ}$  in the temperatures of estimation and of calibration involves an error of 1%. The error due to shifting of the central white or achromatic fringe was investigated by Adams (A., 1915, ii, 478).

Typical illustrations are given of the use of the instrument for air-carbon dioxide mixtures. It may also be employed for the analysis of flue gases and the determination of helium in mixtures.

A table is given showing the relative sensitiveness of the interferometer for different gases.

W. J. W.

**Improved Orsat Apparatus for Gas Analysis.** G. W. JONES and F. R. NEUMEISTER (*Chem. and Min. Eng.*, 1919, 21, 734—736).—The modification of Orsat's apparatus used by the Bureau of Mines, U.S.A., has a Jager's copper oxide tube for the removal of hydrogen and carbon monoxide. The gas burette can be put in communication either with the Orsat pipettes, containing the usual reagents for carbon dioxide, unsaturated hydrocarbons, and oxygen, or with a compensator of the Petersen type, the mercury in which forms contact with a platinum wire and lights a lamp, when the levelling bulb is raised or lowered, and thus facilitates the reading of the level. The copper oxide tube above the Orsat bulbs is heated by means of an electrical heater, which is lowered over it, and then rests on supports. For the determination of hydrocarbons in a gas, a combustion is made in the combustion pipette with a measured quantity of oxygen, the pipette being cooled by compressed air to prevent breakage, and the amounts of the two predominating hydrocarbons are calculated by means of the usual formulæ from the total contraction and amount of carbon dioxide found after the combustion. [See, further, *J. Soc. Chem. Ind.*, 1920, 138A.]

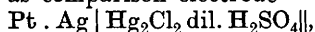
C. A. M.

**Theory of Electrometric Titration.** W. D. TREADWELL (*Helv. Chim. Acta*, 1919, 2, 672—680).—A theoretical paper in which the determination of the end-point in the titration of silver solutions is considered. The method consists in measuring the terminal voltage between a standard silver chloride cell and a silver electrode immersed in the solution, the end-point being that at which the voltage becomes zero. The theory is considered for the titration of solutions of pure silver salts and of the case where there is a quantity of other substances present.

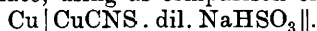
J. F. S.

**Electrometric Titration.** W. D. TREADWELL and L. WEISS (*Helv. Chim. Acta*, 1919, 2, 680—697).—It is shown that the end-

point of many titrations may be determined electrometrically by measuring the terminal voltage between a metal electrode, which is immersed in the solution being titrated, and is capable of sending the same ions into the solution, and a comparison electrode made of the same metal and the insoluble precipitate or product produced in the titration. The two terminals are directly connected with a voltmeter, and the point of zero potential is the end-point of the titration, that is, the point at which the concentration of the metal ions is the same in both the solution being titrated and the comparison electrode. It is essential that during the titration the liquid should be rapidly stirred, and the authors describe an apparatus in which the comparison electrode is built up in the stirrer. In the case of silver solutions, the comparison electrode is  $\text{Ag}|\text{AgCl sat.}|$ , a silver wire furnishes the electrode in the solution, and the titration is carried out with standard sodium chloride. The results are extraordinarily good. In the presence of foreign substances the titration values are too low, but they may be corrected from the course of the titration curve. Hydrogen sulphide may be titrated with silver ions, using as comparison electrode the combination  $\text{Ag}|\text{Ag}_2\text{S. dil. NaNO}_3||$ . Mercurous ions may be titrated by chloride ions, using as comparison electrode



and a similar silver-plated platinum wire as titration electrode. Better results are obtained if the titration is carried out with bromide ions and the calomel in the comparison electrode substituted by mercurous bromide. Copper ions may be titrated by ammonium thiocyanate, using as comparison electrode



In the foregoing cases soluble electrodes have been employed; further experiments were made with insoluble electrodes, and it is found that zinc ions may be titrated with ferrocyanide ion, using as titration electrode a platinum gauze and as comparison electrode  $\text{Pt}|\text{Zn}_2\text{Fe}(\text{CN})_6. \text{HCl}(5 \text{ c.c. in } 300\text{H}_2\text{O})||$ . The titration in this case is carried out at  $70^\circ$ . Ferrous chloride may be titrated with potassium dichromate, using an already completed titration as the comparison electrode and platinum wires in both solutions. This titration is also carried out in warm solutions. Uranous ions may be titrated with potassium permanganate in warm solution, using platinum wires and a uranyl solution as the comparison electrode. Vanadyl solutions may be similarly titrated with permanganate, using platinum wires and a vanadate solution as comparison electrode. In the case of the hydrogen-ion titration, the electrode is too slow in its action for the method as at present constituted to give sharp results.

J. F. S.

**Electrometric Titration.** J. PINKHOF (*Chem. Weekblad*, 1919, 16, 1163—1167).—The investigation concerned the selection of a constant electrode which should have the same potential as the electrode of the liquid at the moment when the end-point was reached. It would then be merely necessary to determine whether the difference of potential of the two electrodes was positive or nega-

tive. To ascertain which compensation electrode is suitable, a potential measurement was made during titration, and when the desired potential was found a combination of electrode and liquid was sought which would give this potential. For the titration of halogens in presence of each other, *N*-potassium bromide is suitable for the compensation electrode in the estimation of the iodine. For the bromine  $\text{Ag-AgCl-0.2NCl}$  is used. In titrating heavy metals with sodium sulphide, a silver-halogen compensation electrode is employed. Titrations of bases with mercuric oxide electrode and the use of the hydrogen electrode are discussed.

W. J. W.

**A Rapid Hydrogen Electrode Method for Determination of Hydrogen-ion Concentrations in Bacterial Cultures or in other Turbid or Coloured Fluids.** HARRY M. JONES (*J. Infect. Dis.*, 1919, **25**, 262—268).—As compared with the colorimetric method, the apparatus described has wider application, is more accurate, less cumbersome, and only slightly less rapid. The hydrogen electrode vessel described was designed to provide a vessel accurate at least to 0.01  $p_{\text{H}}$  and to give a rapid saturation with hydrogen gas, and yet one which is easily constructed. A rapid and labour-saving technique combining the indicator and the gas-chain methods is described, which obviates the difficult task of preparing standard solution for the former method, and of making needless repetitions by the latter.

CHEMICAL ABSTRACTS.

**Iodometric Estimation of Acids.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1920, **57**, 53—68).—The author has investigated the iodometric method, especially with reference to weak acids. The influence of dilution in the case of strong acids, of catalysts, and of a variation in the amount of potassium iodide added, was determined. Tests were carried out with hydrogen chloride, tartaric acid, citric acid, lactic acid, malic acid, succinic acid, acetic acid, formic acid, benzoic acid, salicylic acid, sodium phosphate, and currant juice. The iodometric method gives excellent results with strong acids, especially if diluted, in which case the reagents, after mixing, must remain for ten minutes before titration. A deficiency of potassium iodide causes inaccuracy. Organic oxy-acids can be accurately estimated if a salt of calcium, magnesium, or zinc is added. For phosphoric acid and weak organic acids, not containing a hydroxy-group, the method is unsuitable, but it may be used in the case of formic acid. The applicability of the method to the estimation of fruit juices requires further investigation.

W. J. W.

**Indirect Electrolytic Estimation of Anions without Platinum Electrodes.** II. E. LASALA (*Anal. Fis. Quim.*, 1919, **17**, 235—247).—A continuation of work already published (*A.*, 1919, ii, 239). The present communication deals also with anions which form insoluble silver salts. These are carbonate, oxalate, ferro- and ferri-cyanide, orthophosphate, arsenate, chromate, and thiocyanate. The anion is precipitated as insoluble silver salt.

This is dissolved in a suitable solvent, and the silver estimated electrolytically with a nickel-plated copper cathode and an iron anode. Satisfactory results were obtained only in the case of carbonate, oxalate, ferro- and ferri-cyanide, and thiocyanate. The method was applied to the separation of chloride and iodide. The precipitated mixed silver haloid is washed with ammonia solution (D 0.92). The silver chloride is electrolysed after the addition of ammonium sulphate. The residual iodide is dissolved in 20% solution of potassium cyanide and electrolysed. A small correction must be applied for the solubility of silver iodide in ammonia solution. W. S. M.

**Electrolytic Estimation of the Halogens. An Indirect Method.** J. H. REEDY (*J. Amer. Chem. Soc.*, 1919, **41**, 1898—1902).

—The decomposition voltage of *N*-sulphuric acid, saturated with silver chloride, between silver coated with silver chloride as anode and bright platinum as cathode is found to be 0.59 volt, which corresponds exactly with the sum of the solution potential of silver (0.52 volt) and the overvoltage of hydrogen on bright platinum (0.07 volt). As long as this limiting voltage of 0.59 volt is not exceeded, the electrolysis of haloid solutions with silver anodes proceeds with the formation of an adherent layer of silver haloid on the anode without precipitation in the solution. With the completion of the deposition of the halogen, silver ions appear in the solution with no break in the continuity of the current and with scarcely any rise in potential. An indirect method of estimation of chlorides, bromides, and iodides is based on the above facts. The principle of the method consists in depositing the halogen on a silver anode under a constant voltage of 0.59 volt; some silver will thereby be lost from the anode. The anode is then dried and weighed, and the silver haloid is reduced to metallic silver and the loss in weight determined, which gives the weight of the halogen. A lead accumulator of large capacity is connected across the ends of a sliding rheostat and a current of *E.M.F.* 0.59 volt tapped off. The electrolysis vessel consists of a beaker of 400 c.c. capacity fitted with an anode of silver gauze, coated with silver electrolytically, and a bright platinum cathode and a stirrer. The electrolysis is carried out with 200 c.c. of solution for about fifteen minutes; the current flowing at first is rather large, but after about fifteen minutes it becomes negligible. The potential is then raised to 0.60 volt for five minutes. The silver electrode with its halogen deposit is washed, dried, and weighed. After weighing, it is made the cathode in a dilute solution of sodium hydroxide and electrolysis carried out until hydrogen is freely liberated from the surface. The silver haloid is thus reduced to black silver, which is not very adherent and must be carefully handled. After a thorough washing, the electrode is heated at 500° in an electric furnace until the deposit is white, and thoroughly sintered together. It is then weighed, and the loss in weight gives the weight of the halogen. The results given in the paper show that the method is quite as good as the usual gravimetric method.

J. F. S.

**Estimation of Bromide in Mineral Waters and Brines.**

W. W. SKINNER and W. F. BAUGHMAN (*Science*, 1919, **50**, 50).—Chromic acid in concentrated solution liberates bromine quantitatively from bromides at the ordinary temperature, and the bromine is removed by aspiration. Only a trace of chlorine is liberated from chlorides. When chromic acid acts on a solution containing chloride and bromide, therefore, the mixture of halogens removed by aspiration is dissolved in a solution of sodium sulphite and hydroxide, which is then evaporated to dryness and the residue again treated with chromic acid solution and aspirated a second time. The double treatment gives very trustworthy results.

## CHEMICAL ABSTRACTS.

**Estimation of Alkali Sulphide in Dilute Solution.** H. G.

BENNETT and W. G. BENNETT (*J. Soc. Leather Trades Chem.*, 1919, **3**, (11), 190—193).—A measured quantity of the solution containing not more than 0.04% of hydrogen sulphide is distilled in an atmosphere of carbon dioxide with an excess of boiling magnesium chloride solution. A current of carbon dioxide carries the liberated hydrogen sulphide into a receiver containing standard iodine solution. A second receiver, containing standard sodium arsenite solution, is arranged to trap any iodine vapour carried over by the gas. The method is accurate under these conditions and provided there are no rubber connections exposed to the iodine vapour. D. W.

**Neutralisation Curve of Sulphurous Acid.** I. M. KOLTHOFF

(*Chem. Weekblad*, 1919, **16**, 1154—1163).—The accuracy of the results when sulphurous acid is titrated with methyl-orange or dimethyl-yellow as indicator depends on the concentration of the hydrogen ions of the sodium hydrogen sulphite, and therefore also on the second dissociation constant of the sulphurous acid. This has been determined from the degree of hydrolysis of solutions of sodium sulphite and found to be  $1 \times 10^{-7}$  at  $15^\circ$ . The hydrogen-ions concentration of a 0.1 mol. sodium hydrogen sulphite solution calculated from the two dissociation constants gave the value  $[H^+] = 3.3 \times 10^{-5}$ . A curve showing the neutralisation of sulphurous acid was constructed. In the titration of sulphurous acid errors of  $\pm 2\%$  and of  $\pm 6\%$  were obtained when the indicators were dimethyl-yellow and phenolphthalein respectively. The addition of sodium chloride reduced the error with phenolphthalein to  $\pm 2\%$ . Accuracy can only be ensured if excess of barium nitrate is added after the pink coloration of the phenolphthalein has appeared, and the titration then continued to the end-point. W. J. W.

**Estimation of Sulphates in the presence of Organic Sulphonic Acids.** T. CALLAN, JAS. A. RUSSELL HENDERSON, and R. BARTON (*J. Soc. Chem. Ind.*, 1919, **38**, 410—411r).

—The solution of the substance (containing about 0.2 gram of sulphate) is rendered slightly ammoniacal (a small quantity of calcium chloride is also added to precipitate any carbonate, which is then separated by filtration), and the mixture is boiled until all excess of ammonia

has been expelled. Twenty c.c. of  $N/4$ -barium chloride solution are then added, the heating continued for a few minutes, and the excess of barium titrated with  $N/4$ -potassium chromate solution, using starch-iodide paper as indicator. A drop of the mixture is placed on the paper, and the edge of the spot is touched with a drop of very dilute hydrochloric acid. A blue colour develops in about ten seconds when an excess of soluble chromate is present. An immediate blue colour indicates that a considerable excess of chromate has been added.

W. P. S.

**Detection of Nitrogen in Organic Compounds by Castellana's Reaction.** J. FLIERINGA (*Pharm. Weekblad*, 1920, 57, 3—4).—Castellana's reaction (A., 1905, ii, 207) may give a positive reaction even in nitrogen-free compounds, owing to combination of atmospheric nitrogen, if the magnesium is in excess. It is preferable to use a mixture of 2 parts of sodium carbonate and 1 part of magnesium. Sodium carbonate containing 1 molecule of  $H_2O$  should be employed. Addition of sugar to the reaction mixture eliminates the error caused by absorption of atmospheric nitrogen.

W. J. W.

**The Relative Accuracy of Colorimetric and Titrimetric Procedures for estimating Nitrogen as Ammonia.** E. R. ALLEN and B. S. DAVISSON (*J. Biol. Chem.*, 1919, 40, 183—197).—It appears that the colorimetric methods are slightly the more accurate. On the other hand, the conditions for accurate titrations may be attained more easily than those for satisfactory Nessler estimations, and at the same time the titrimetric methods are applicable to a wide range of nitrogen values. The chief disadvantage of the Nessler process is the fact that the reaction is imperfectly understood, and the appearance of clouds and precipitates difficult to avoid. Again, it is believed that the personal error is greater in colorimetric methods than in titrimetric methods. The general conclusion is therefore in favour of the titrimetric methods.

J. C. D.

**Estimation of Nitrogen in Nitrates.** F. PILZ (*Zeitsch landw. Vers.-Wesen Deutschösterr.*, 1919, 22, 180—188; from *Chem. Zentr.*, 1919, iv, 767).—Comparative estimations of nitrogen in nitrates by various methods showed that reduction with Devarda's alloy yielded the most trustworthy results, and is to be recommended more than the method described by Arnd (A., 1917, ii, 504). Busch's method (A., 1905, ii, 418) is less trustworthy. Other methods investigated were the one proposed by Ulsch (reduction in acid solution with iron powder) and the indirect method (conversion of the nitrate into chloride).

W. P. S.

**Method for the Estimation of Minute Quantities of Nitrogen in Organic Substances, which furnishes a New Quantitative Method of Diagnosis in some cases of Mental Disease.** R. V. STANFORD (*Rep. Chem. Lab. Cardiff City Mental Hospt.*, 1919, No. 2. Compare A., 1913, i, 930).—A small quantity

of the organic substance, as, for example, 1 c.c. of cerebrospinal fluid, is oxidised by the Kjeldahl process in the usual manner. The subsequent distillation is carried out in the ordinary apparatus, but the distillate is collected in three fractions in Nessler cylinders. The third fraction should show little or no coloration with Nessler's reagent. The colour produced by the first two fractions is compared in the usual manner with that produced by a standard solution of ammonium chloride. Considerable care has to be taken to avoid errors arising from ammonia in the reagents and apparatus.

The author records a number of analyses of cerebrospinal fluid from mental cases. The "nitrogen number," that is, the number of hundredths of a milligram of total nitrogen contained in 1 c.c. of cerebrospinal fluid, may be of value in diagnosis. On the whole, density and nitrogen number of the fluids run parallel to one another.

No traces of choline and only the merest traces of ammonium salt were detected in the cerebrospinal fluid in mental disease.

J. C. D.

**Process for the Estimation of Arsenic. Chemistry of the Marsh-Berzelius Process.** B. S. EVANS (*Analyst*, 1920, 45, 8—17).—The arsenic is evolved as hydrogen arsenide, in the same way as in the ordinary Marsh-Berzelius test, but is conducted over a roll of red-hot copper, which retains the arsenic, the amount of which is obtained from the increased weight of the copper. The compound formed with the copper usually melts and resembles solder in appearance, but occasionally brilliant, silvery-white, blade-shaped crystals are produced. Analyses of the deposits gave 67.5 and 70.5% of copper and 32.28 and 29.27% of arsenic, and thus appeared to be mixtures of the arsenides  $\text{Cu}_3\text{As}$  and  $\text{Cu}_5\text{As}_2$ . The results obtained with elementary arsenic and various arsenic compounds were invariably 1.4% too low, and the cause of this loss could not be definitely traced, although the results indicated that if the arsenic remained in the flask, it was in the form of a very stable complex. In order to prevent separation of elementary arsenic, it is advisable that the amount of substance introduced should contain considerably less than 0.5 gram of arsenic. [See also *J. Soc. Chem. Ind.*, 1920, February.] C. A. M.

**Estimation of Arsenic in Tin and Tinnings.** LUCIEN VALLERY (*Compt. rend.*, 1919, 169, 1400—1402).—Marsh's method is liable to give results which may, in some cases, be wrong to the extent of 75% of the amount found when applied to the estimation of arsenic in tin. The author recommends that the arsenic should be distilled off as arsenic chloride by Hollard and Bertiaux's method, and the arsenic estimated colorimetrically in the distillate after reduction to colloidal arsenic by means of hypophosphorous acid. In this way, the results obtained are accurate to within 3% of the total at a concentration of 1 in 100,000. W. G.

**New Method of Estimation of Carbon and Hydrogen in Organic Substances.** KUNIIKO SUMIKURA (*J. Tokyo Chem. Soc.*, 1919, **40**, 593—606).—The essential point of the method is the combined use of platinum and cerium dioxide. (1) *Substances containing Carbon, Hydrogen (and Oxygen) only.*—An ordinary combustion tube is filled, in order, with cerium dioxide (5 cm.), porcelain boat, cerium dioxide (8 cm.) (only one burner is necessary under each of these), and a coil of platinum or platinum-iridium wire (2 m.), which is electrically heated with adjustable resistances. The wire is first heated in a separate tube before being placed in the combustion tube. The cerium dioxide is prepared by heating copper gauze packed with asbestos soaked in a solution of ceric nitrate.

(2) *Substances containing Nitrogen and Sulphur.*—Lead dioxide is placed between the second cerium dioxide gauze and the platinum coil, and is heated at 300—350°. (3) *Substances containing Halogens.*—Silver foil is placed between the second cerium dioxide gauze and the platinum wire. If nitrogen is also present, lead dioxide is placed between the silver foil and the platinum wire, and is heated at 300—320°. (4) *Substances containing Phosphorus.*—Lead monoxide is mixed with the substance. Trustworthy results are recorded.

CHEMICAL ABSTRACTS.

**Rapid Estimation of Carbon Monoxide in Air.** ARTHUR B. LAMB and ALFRED T. LARSON (*J. Amer. Chem. Soc.*, 1919, **41**, 1908—1920).—Two methods for the rapid estimation of small quantities of carbon monoxide in air are described. In the first method, the gas is passed over a platinum wire heated to redness, and the carbon monoxide partly burned in contact with it. The gas then passes over heated copper oxide, where the carbon monoxide is completely burnt; it then passes through a spiral contained in a thermostat to bring it to its original temperature, and finally over a second exactly similar platinum wire heated by the same current as the first. The two platinum wires are made arms of a Wheatstone bridge, and since the first wire will necessarily be hotter than the second, they will have different resistances. The change in the resistance of the first wire gives a measure of the carbon monoxide concentration. In the second method, the mixture is passed through a platinised platinum catalyst, when the carbon monoxide is completely burnt. The temperature change is measured by a thermo-element, and indicates the concentration of carbon monoxide. Both methods are rapid, and the latter is particularly accurate, easy to instal and to operate. The catalyst, with reasonable precautions, remains active for many weeks.

J. F. S.

**Apparatus for the Volumetric Estimation of Small Quantities of Carbon Dioxide by Displacement from Liquids by means of a Rapid Current of Air at the Ordinary Temperature and Pressure.** A. COSTANTINO (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 118—121).—In the apparatus described, which



consists of a closed system, a rotary mineral oil pump causes the repeated circulation of purified air, first through the liquid containing the carbon dioxide, and then through a definite volume of standard barium hydroxide solution, this being subsequently titrated with acid in presence of phenolphthalein. The determination occupies in all about forty-five minutes. Test experiments with sodium carbonate solutions containing 6.4—21 mg. of carbon dioxide show that the method yields accurate results. T. H. P.

**Estimation of Metals by Electrolytic Deposition without using an External Supply of Electricity.** MAURICE FRANCOIS (*Ann. Chim.*, 1919, [ix], 12, 178—192).—A more detailed account of work already published (see A., 1919, ii, 34). W. G.

**Use of Nickel Crucibles for the J. Lawrence Smith Method in Estimating Soil Potassium.** SETH S. WALKER (*J. Ind. Eng. Chem.*, 1919, 11, 1139—1140).—The same results are obtained whether platinum or nickel crucibles are used for the heating of the soil with ammonium chloride and calcium carbonate, but the nickel crucible is attacked by the mixture and the life of the crucible is short. W. P. S.

**The McCrudden Gravimetric Calcium Method Modified.** J. P. HALVERSON and J. A. SCHULZ (*J. Ind. Eng. Chem.*, 1920, 12, 77—78).—The calcium oxalate precipitate is collected on a filter of specially prepared asbestos contained in a Gooch crucible; after washing, both filter and precipitate are mixed with water, acidified with sulphuric acid, and titrated at 65° with permanganate solution. The filter is prepared by digesting ignited asbestos with dilute sulphuric acid and a slight excess of permanganate for one hour at 60° to 70°, and then washing it until free from acid. [See, further, *J. Soc. Chem. Ind.*, 1920, February.] W. P. S.

**Estimation of the Calcium Oxide Content of Milk of Lime.** GEORG LENART (*Zeitsch. Ver. deut. Zuckerind.*, 1919, 1—15, 360—361).—Mategček's table (*Österr.-Ungar. Zeitsch. Zuckerind.*, 1871, 12, 718) correlating the sp. gr. and calcium oxide content of milk of lime is regarded as far from correct, whilst that published by Lunge and Blattner (*Dingl. Polytechn. J.*, 1883, 466) is also considered to be untrustworthy. Experiments are described demonstrating the difficulty of obtaining exact results by means of the hydrometer (the method of density determination adopted in the construction of the second table), since the readings are influenced by the shape and length of the spindle, by the width and depth of the column of liquid in the cylinder, and also by the degree of movement imparted to the liquid at the moment of observation. Using a pycnometer consisting simply of a cylindrical vessel having a capacity of about 500 c.c., provided with a ground-glass plate as cover, a new table has been constructed by the author in which the density values range from 1.0085 to 1.2195 (1.5° to 26.2° Bé.)

at 20°, temperature corrections being stated for readings made between 20° and 40°. Milk of lime which has been vigorously shaken for about two hours assumes a viscous condition, in which the particles remain almost completely in suspension for some days, this being believed to be due to the formation of a hydrated compound, probably  $\text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$ , to which attention has already been directed by Herzfeld (*Zeitsch. Ver. deut. Zuckerind.*, 1897, 817) and by Karcz (*Chem. Zeit.*, 1898, 22, 38). J. P. O.

**The Permanganate Method for Copper.** LOUIS F. CLARK (*J. Ind. Eng. Chem.*, 1919, 11, 1138—1139).—A modification of the procedure for the titration of cuprous thiocyanate with permanganate solution is proposed, with the object of making the estimation less arbitrary. The cuprous thiocyanate precipitate is treated in a beaker with 25 c.c. of hot 4% sodium hydroxide solution until the precipitate is decomposed, 25 c.c. of cold 15% sulphuric acid and a quantity of 1% ferric sulphate (anhydrous salt) solution are added, and the mixture is titrated with permanganate solution. Towards the end of the titration, and when the mixture becomes whiter in colour, 5 c.c. of concentrated hydrochloric acid are added, and the titration then completed. Under these conditions, 6 atoms of copper should be equivalent to 7 atoms of iron, or a ratio factor of 0.1626; the ratio factor actually found as the result of experiment is 0.1646. [See, further, *J. Soc. Chem. Ind.*, 1920, 138A.] W. P. S.

**Microchemical Identification of Soluble and Insoluble Mercury Compounds.** G. DENIGÈS (*Bull. Soc. Pharm. Bordeaux*, 1919; from *Ann. Chim. anal.*, 1919, [ii], 1, 383—385).—The tests depend on the characteristic crystals obtained when a small quantity of the compound is treated with a drop of potassium bromide-iodide solution. Mercurous compounds and mercuric cyanide are oxidised previously with bromine. Mercuric iodide itself is identified by the crystals obtained from its alcohol or acetone solution. W. P. S.

**Volumetric Estimation of Mercuric Chloride.** OTTO SASSE (*Pharm. Zeit.*, 1919, 64, 633).—Referring to the method described by Utz (*A.*, 1919, ii, 428), the author mentions that he himself had published a method (*Pharm. Zeit.*, 1887) for the volumetric estimation of mercuric chloride; this method depends on a titration with potassium iodide solution, and is trustworthy. W. P. S.

**Application of Rotating Reductors in the Estimation of Iron.** WALTER SCOTT (*J. Ind. Eng. Chem.*, 1919, 11, 1135—1137).—Gooch and the author have shown previously (*A.*, 1918, ii, 373) that vanadic acid may be reduced by rapidly rotating anodes of silver or copper, and the author now describes a similar method of reduction for ferric salts. The latter in sulphuric acid solution are reduced completely by rotating reductors of zinc or aluminium, with or without the use of an external current. W. P. S.

**A Sensitive Reaction for Manganese.** P. H. HERMANS (*Pharm. Weekblad*, 1919, **56**, 1344—1346).—Caron and Raquet's reaction for manganese (*Rép. Pharm.*, 1919, 97) was independently discovered by the author, and was, in addition, utilised as a test for nitrogen tetroxide and for nitrites. All oxidising agents are not effective in promoting the red coloration, for example, hydrogen peroxide, potassium persulphate, chlorine, bromine, iodine, chloric acid, iodic acid, potassium ferricyanide, but addition to them of 0.5% solution of osmic acid produces a satisfactory result. Active oxidising agents for the test are bleaching powder, potassium permanganate, and dichromate, lead peroxide, cerium ammonium nitrate, nitrous acid, and nitrogen tetroxide.

Lead peroxide is most suitable for the manganese test. The reaction is sensitive to 0.07 mg. manganese or 0.03 mg. sodium nitrite per c.c. of solution.

The red coloration is considered to be a complex alkali manganese oxalate.  
W. J. W.

**Indirect Detection of Tin.** FR. FEIGL (*Chem. Zeit.*, 1919, **43**, 861).—Ferrous salts give a red precipitate with an ammoniacal solution of dimethylglyoxime, but the presence of ferric salts, which give a precipitate of ferric hydroxide with the reagent, interferes with the test. The precipitation of ferric iron as hydroxide and of ferrous iron as ferrous dimethylglyoxime may be prevented by adding an organic hydroxylated compound, such as citric or tartaric acids or potassium sodium tartrate, and the ferrous ion then gives a carmine-red solution. In each case, complex iron compounds are formed. In using this reaction as a sensitive indirect test for tin, the mixed sulphides, presumably of antimony and tin, are dissolved in hydrochloric acid, and one portion of the solution is tested for antimony with iron wire. In a second portion, the tin and antimony are precipitated by means of pure zinc, and the tin extracted from the deposit by means of concentrated hydrochloric acid. The solution is poured into a hot dilute solution of ferric chloride, a little citric acid or potassium sodium tartrate added, and the liquid tested with ammoniacal alcoholic dimethylglyoxime solution. The ferrous ion formed by reduction with the stannous ion will give a red coloration, the intensity of which is proportional to the amount of stannous chloride.  
C. A. M.

**Estimation of Thiophen in Industrial Benzenes.** ANDRÉ MEYER (*Compt. rend.*, 1919, **169**, 1402—1404).—A modification of Denigès's method (compare A., 1895, ii, 332, 372). Denigès's reagent is prepared by dissolving 50 grams of mercuric oxide in 200 c.c. of sulphuric acid diluted with 1000 c.c. of water. Twenty c.c. of this reagent are mixed with 75 c.c. of methyl alcohol and 5 c.c. of the benzene under examination in a stoppered bottle. The mixture is shaken from time to time, and, after thirty minutes, is filtered. Ten c.c. of the filtrate are diluted with 20 c.c. of water, a few drops of nitric acid are added, and the whole is titrated with

*N*/10-ammonium thiocyanate solution, using 1 c.c. of a 20% iron ammonium alum solution as indicator. In view of the possible presence of acetone in the methyl alcohol, a blank experiment is conducted, using pure benzene free from thiophen. The difference between the two titrations is a measure of the mercury precipitated by the thiophen as the compound,  $(\text{HgO})_2\text{SO}_4\cdot\text{HgSC}_4\text{H}_4$ , and the factor for the conversion of mercury to thiophen is 0.14. W. G.

**Titration and Partial Reduction of Nitro-compounds with Titanous Chloride.** C. F. VAN DUIN (*Chem. Weekblad*. 1919, 16, 1111—1122).—An examination of the titanous chloride method for the titration of nitro-compounds. The constancy of titre of a titanous chloride solution at the ordinary temperatures and after heating was especially investigated; also the general applicability of the method to various classes of nitro-compounds. At the ordinary temperatures, only slight variations in titre were found after keeping for several days. Titration experiments before and after heating the titanous chloride solution were carried out in comparable conditions in presence of alcohol, hydrochloric acid, and acetic acid. It was found that the assumption of an invariable titre during the heating of the titanous chloride solution led to quite erroneous results. The error is small in presence of acids, especially in hydrochloric acid, tolerable results being only obtained in strongly acid solutions. From experiments with picric acid, *m*-dinitrobenzene, and *s*-trinitrotoluene, the author concludes that the method yields results of the same order of accuracy as the Dumas method. The reduction and titration of the following classes of nitro-compounds were carried out: nitroamines (*s*-trinitrophenylmethylnitroamine, aminotrinitrophenylmethylnitroamine, trinitromethylnitroaminophenol, trinitromethylnitroaminoanisole, trinitrodimethyldinitroaminobenzene), tetranitro-compounds (tetranitrophenol, tetranitrophenylmethylnitroamine, tetranitroaniline), and hexanitro-compounds with two nuclei (hexanitrodiphenyl sulphide, hexanitrodiphenylsulphone). In the reduction of nitroamines, side reactions may take place in which the nitroamino-group is entirely removed from the nucleus. In all cases, blank experiments must be carried out in order to estimate the alteration in the titanous chloride solution on heating. The amount of excess of the solution necessary for complete reduction must also be determined in each case. Only in those conditions can this method of nitrogen analysis be considered superior to that of Dumas.

W. S. M.

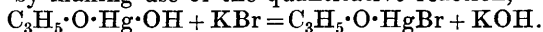
**Detection of Methyl Alcohol in Ethyl Alcohol.** M. POLINSKI (*Chem. Analyst*, 1919, 28, 11).—Five c.c. of the sample are distilled with 50 c.c. of water and 3 grams of sodium persulphate, the distillate being collected in fractions of 2 c.c. each. The fifth fraction is treated with eight drops of a freshly prepared, filtered 1% solution of phenylhydrazine hydrochloride, four drops of 5%

potassium ferrocyanide, and 1 c.c. of concentrated hydrochloric acid. A pink coloration is produced if methyl alcohol is present.

CHEMICAL ABSTRACTS.

**Complex Organic Mercury Compounds.** EINAR BILLMANN (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 12, 1—11).—The complex compound formed from allyl alcohol and mercuric acetate is very stable, the concentration of the mercuric ion in a 1/160-molar solution being only  $10^{-8.40}$  (compare A., 1917, i, 123). This fact can be made use of in the electrometric estimation of allyl alcohol. The aqueous solution of allyl alcohol is put in a beaker containing mercury, which forms one electrode, the other being a calomel electrode. A standard solution of mercuric acetate is then run in, and the *E.M.F.* curve plotted. The point of inflexion on the curve is very sharp, and accurate results are obtained.

Allyl alcohol can also be estimated by adding mercuric acetate and potassium bromide to the solution, and titrating the acetic acid set free, with phenolphthalein as indicator. The liberation of acetic acid is quantitative, according to the equations:  $C_3H_5 \cdot OH + Hg(OAc)_2 = C_3H_5 \cdot O \cdot Hg \cdot OAc + AcOH$ ;  $C_3H_5 \cdot O \cdot Hg \cdot OAc + KBr = C_3H_5 \cdot O \cdot HgBr + OAcK$ . Mercury can also be estimated very accurately by making use of the quantitative reaction,



A weighed quantity of mercuric oxide is dissolved in 5*N*-sulphuric or nitric acid; the solution is diluted with water free from carbon dioxide, a few c.c. of allyl alcohol added, and then *N*/5-sodium hydroxide until the liquid is alkaline to phenolphthalein. The whole is then exactly neutralised with *N*/5-sulphuric acid, 5 grams of potassium bromide added, and the liquid well shaken to give a solution, the entrance of carbon dioxide being carefully excluded. The liberated alkali is then titrated. Halogen acids must not be present in estimations according to this method.

Maleic and crotonic acids do not give sufficiently stable complexes for estimation by the above methods, but *allocinnamic* acid gives good results with the mercuric acetate-potassium bromide method. Cinnamic acid also gives mercury complexes, and is to be reported on later.

Mercury can be readily and accurately estimated by a modification of Ince's method (A., 1917, ii, 327). To the solution of the mercuric salt, or of mercuric oxide in nitric or sulphuric acid, is added a large excess of alkali; the whole is then exactly neutralised with standard acid, using phenolphthalein as indicator. Potassium iodide (5 grams) is then added, and the liberated alkali carefully titrated, carbon dioxide being excluded. T. S. P.

**Titration of Organic Acids in Urine.** D. D. VAN SLYKE and W. W. PALMER (*Proc. Soc. Exp. Biol. Med.*, 1919, **16**, 140—141).—Carbonates and phosphates are removed by adding 2 grams of calcium hydroxide to 100 c.c. of urine and filtering after ten minutes. The acidity of 25 c.c. of the filtrate is brought to  $p_H = 8$

(circa) by adding 0.2*N*-hydrochloric acid until the pink colour of phenolphthalein disappears, 5 c.c. of 0.02% Tropæolin OO are added, and the solution is titrated to  $p_H=2.7$  with 0.2*N*-hydrochloric acid, the volume being brought to approximately 50 c.c. by the addition of water towards the end of the titration. The colour is compared with that of 50 c.c. of a control solution with the same  $p_H$  value and indicator. The amount of 0.2*N*-hydrochloric acid required to give the end-point with a control in which water replaces urine is subtracted. The titration estimates from 93% to 100% of each of the organic acids known to be present in urine in quantitatively significant amounts. It also includes very weak bases, but of this class of substances only creatine and creatinine, which are estimated to nearly 100%, are significant. The titration figure, corrected for the amounts of these two bases, represents the organic acids in urine. CHEMICAL ABSTRACTS.

**Detection of  $\beta$ -Hydroxybutyric Acid, Acetoacetic Acid, and Acetone in Urine.** R. LILLIG (*Pharm. Zeit.*, 1919, **64**, 696—697, 707—709).—A collection of some sixty methods which have been proposed for the purpose; a brief description is given of each method. W. P. S.

**Bellier's Reaction for Vegetable Oils.** A. VAN RAALTE (*Chem. Weekblad*, 1919, **16**, 959—960).—The benzene used for this reagent must be free from thiophen, otherwise a dirty green, instead of a violet, coloration is obtained. W. J. W.

**Relative Sensitiveness of the Fehling, Phenylhydrazine, and Nylander Tests for the Detection of Dextrose in Urine.** GEORGE E. ÉWE (*Amer. J. Pharm.*, 1919, **91**, 717—719).—Fehling's test is the most sensitive of the three tests investigated; it yields a reaction with a solution containing 0.00125% of dextrose. The phenylhydrazine test is also sensitive, giving a reaction, after two hours, with a 0.0025% solution of dextrose, but the Nylander reagent (potassium sodium tartrate, 4 grams; 10% sodium hydroxide solution, 100 c.c.; bismuth subnitrate, 2 grams) fails to give a reaction unless the solution contains at least 0.5% of dextrose. W. P. S.

**Titration of Sugars.** E. SCHOWALTER (*Zeitsch. Nahr. Genussm.*, 1919, **38**, 221—227).—A reply to Rupp and Lehmann (A., 1919, ii, 434); the author maintains the correctness of his former remarks (A., 1919, ii, 172). W. P. S.

**The Isaacson Method for Estimating Dextrose.** ELISABETTA C. PENNELL (*J. Lab. Clin. Med.*, 1919, **4**, 736—737).—Isaacson's method (A., 1918, ii, 246) was found highly untrustworthy when compared with the Fehling volumetric method.

CHEMICAL ABSTRACTS.

**Separation of Dextrose and Lævulose.** FRANZ LUCIUS (*Zeitsch. Nahr. Genussm.*, 1919, **38**, 177—185).—A method for the estimation of dextrose in the presence of lævulose depends on the fact that the rotation of the latter is destroyed by heating for seven

hours with dilute hydrochloric acid, whilst that of dextrose is not affected. Fifty c.c. of the sugar solution (containing from 2 to 4% of the sugars) are mixed with 10 c.c. of 5*N*-hydrochloric acid and heated in a boiling water-bath for seven hours. The mixture is then nearly neutralised with sodium hydroxide solution, diluted to 100 c.c., treated with animal charcoal and filtered, if necessary, and polarised at 20°. About 99% of the dextrose actually present is found. The dextrose remaining after the acid treatment cannot be estimated by determining the copper-reducing power of the solution as the lævulose is converted into reducing substances, which, however, are optically inactive.

W. P. S.

**Separation of "Saccharin" from Benzoic Acid.** E. SCHOWALTER (*Zeitsch. Nahr. Genussm.*, 1919, **38**, 185—194).—The presence of "saccharin" interferes with the estimation of benzoic acid in foods, etc., by the methods described by Mohler, von der Heide, and Grossfeld (*A.*, 1908, ii, 906; 1910, ii, 359; 1915, ii, 848), but the two substances may be separated from one another by taking advantage of the insolubility of "saccharin" in carbon tetrachloride. The residue obtained on evaporating the ethereal solution of the two substances at a low temperature is dried under reduced pressure to remove the last traces of ether and acetic acid, and is then treated with carbon tetrachloride; the benzoic acid dissolved by this solvent may be estimated by titration and the insoluble "saccharin" identified by Klostermann and Scholta's reaction (*A.*, 1916, ii, 586). Separation of the two substances between sublimation is untrustworthy; "saccharin" begins to sublime at 120° and 130°. Animal charcoal absorbs considerable quantities of "saccharin," its anhydride and sodium salt, as well as benzoic acid and benzoates, from an aqueous solution.

W. P. S.

**Estimation of *p*-Phenylenediamine.** T. CALLAN and JAS. A. RUSSELL HENDERSON (*J. Soc. Chem. Ind.*, 1919, **38**, 408—410T).—A modification of a method described by Effront (*A.*, 1905, ii, 60) is recommended. Fifty c.c. of sodium hypochlorite solution, containing 12—15% of available chlorine, are diluted to 1 litre, and 100 c.c. of this solution are diluted with an equal volume of water, 1 gram of sodium carbonate is added, followed by 10 c.c. of the *p*-phenylenediamine solution (in dilute hydrochloric acid); the latter solution should contain from 2 to 6% of the substance, and the addition should be made gradually with constant stirring. Benzoquinonedichloroimide is precipitated as a white substance and, without filtration, the excess of chlorine in the mixture is titrated with *N*/10-sodium arsenite solution. The difference between this titration and the quantity of arsenite solution required for the titration of the hypochlorite solution itself is equivalent to the amount of chlorine removed from solution as dichloroimide; 1 c.c. of *N*/10-arsenite solution therefore corresponds with 0.0018 gram of *p*-phenylenediamine. The method may also be used for the estimation of *p*-nitroaniline, *p*-aminodiphenylamine, benzidine, and naphthylene-1:4-diamine, but with the latter the yield found is

only 98—99% of the quantity of substance present owing to the slight solubility of the dichloroimide formed. The method is not applicable to substances containing a sulphonic group, since these give soluble dichloroimides.

W. P. S.

**Estimation of Carbamide in Blood and Urine.** H. CITRON (*Deut. med. Woch.*, 1919, **45**, 975; from *Chem. Zentr.*, 1919, iv, 719).—A reply to Brahm (this vol., ii, 66).

H. W.

**Electrometric Method for the Estimation of Ferrocyanides depending on a Change in Oxidation Potential.** G. L. KELLEY and R. T. BOHN (*J. Amer. Chem. Soc.*, 1919, **41**, 1776—1783).—Solutions of ferrocyanides may be estimated by titration with potassium permanganate in the presence of sulphuric acid, using the sudden change in *E.M.F.* observed with a bright platinum electrode to mark the end-point. The method is as follows: About 1 gram of potassium ferrocyanide in 250 c.c. of water and 2.5—5.0 c.c. of sulphuric acid (*D* 1.58) is titrated with 0.05*N*-potassium permanganate, using an electrometric apparatus which will indicate changes of potential of the order of one millivolt (*A.*, 1917, ii, 512). A small precipitate may form during the titration, but this will redissolve. The titration should be performed slowly with mechanical stirring. As the end-point is approached the permanganate should be added drop by drop, and time allowed for the completion of the reaction. The end-point is taken as the point of greatest change in potential for equal additions of permanganate. Should too much permanganate be added, the end-point may be approached from the other side by adding a standard solution of ferrocyanide. The presence of ferricyanides does not interfere with the titration, neither do amounts of chloride up to 1 gram of sodium chloride. Any salts which under the conditions of experiment produce a precipitate with either ferrocyanide or ferricyanide seriously interfere with the method.

J. F. S.

**Use of Silicotungstic Acid in the Estimation of Alkaloids.** ERWIN TAIGNER (*Zeitsch. anal. Chem.*, 1919, **58**, 346—352).—Silicotungstic acid solution may be used for the quantitative precipitation of atropine, strychnine, and cocaine from their hydrochloric acid solutions; the precipitates formed are collected, after the addition of sodium chloride, washed with 1% hydrochloric acid, dried at 40°, and weighed. The precipitates have the general formula  $12\text{WO}_3, \text{SiO}_2, 2\text{H}_2\text{O}, 4\text{-alkaloid}$ .

W. P. S.

**Colour Reactions of Emetine.** ABEL LAHILLE (*Arch. méd. exp.*, **27**, 296; *Zentr. Biochem. Biophys.*, 1919, **20**, 398).—Emetine hydrochloride develops a yellow coloration with calcium chloride and with concentrated nitric acid. When a small crystal of ammonium molybdate is added to a solution of the hydrochloride in concentrated sulphuric acid a green zone, which subsequently turns blue, is formed round the crystal; the colour disappears on dilution



with water and reappears on heating. A green coloration is produced when a dichromate is used instead of ammonium molybdate.

CHEMICAL ABSTRACTS.

**The Arsenotungstic Reagent in the Method of Bertrand and Javillier for the Estimation of Nicotine.** LUIS GUGLIAMELLI and ULAUS HORDH (*Anal. Soc. Quim. Argentina*, 1919, 7, 121—123).—The preparation of silicotungstic acid for the estimation of nicotine by the method of Bertrand and Javellier (A., 1909, ii, 450) presents difficulties. The authors recommend the use of arsenotungstic acid (Guglielmelli, A., 1916, ii, 584, 587) as a precipitant. The procedure is otherwise unaltered. W. S. M.

**Ehrlich's Reaction with *p*-Dimethylaminobenzaldehyde and Urorosein.** E. SALKOWSKI (*Biochem. Zeitsch.*, 1919, 97, 123—129).—The reaction of *p*-dimethylaminobenzaldehyde with indole, indoleacetic, indolepropionic and indoleaminopropionic acids is described and discussed. Herter's theory concerning the origin of uroscopin in urine is also discussed. S. S. Z.

**Estimation of Tyrosine by means of Millon's Reaction.** MORIZ WEISS (*Biochem. Zeitsch.*, 1919, 97, 170—176).—A 1/50,000 solution of tyrosine to which Millon's reagent is added is used as a standard. The solution to be examined is then diluted until it gives with Millon's reagent a coloration equal to that of the standard. The method can be employed for the estimation of tyrosine in the products of hydrolysis of proteins. S. S. Z.

**New Method of Estimating Albumin in Urine.** DOMENICO GANASSINI and PIETRO FABBRI (*Boll. Chim. Farm.*, 1919, 58, 313—319).—A method of estimating albumin in urine is based on the fact that the sulphur of the cystinic group in the protein molecule is readily detached by the action of hot alkali hydroxide, and in presence of lead plumbite yields lead sulphide. On then titrating the liquid with iodine solution, the metaproteins are first oxidised and iodised, and the lead sulphide is then converted into lead sulphate. In applying the method, from 20 to 100 c.c. of urine (according to the amount of albumin indicated by a preliminary test) are mixed with 5% of sodium dihydrogen phosphate (to prevent precipitation of phosphates of alkaline earth metals), and the liquid heated and stirred for a few seconds until the albumin has coagulated. The precipitate is separated, washed, and dissolved in 10 to 30 c.c. of 10% potassium hydroxide solution, from 3.3 to 10 c.c. of 5% normal lead acetate solution added, and the beaker immersed for five minutes in boiling water. The liquid is then cooled to 21° and titrated with *N*/10-iodine solution, which is added at the rate of two drops per second, with continual stirring, until the liquid becomes colourless. The number of c.c. of iodine multiplied by 0.0330 gives the quantity of albumin in the amount of urine taken. Standard potassium ferricyanide solution may be used instead of iodine solution for the titration, but the end-point of the reaction is not so sharp. C. A. M.

**Medical Analysis of Urine by the Combined Use of Tungstic Acid and Other Reagents.** HUGH CAMPBELL ROSS (Brit. Pat., 134710).—When to 2 c.c. of urine 0.2 c.c. of a reagent composed of a 12% aqueous solution of colloidal tungstic acid to which 10% of acetic or tartaric acid to neutralise any possible alkalinity of the urine, and 2.5% of sodium potassium tartrate have been added, the presence of albumin is indicated by the formation of a precipitate which does not dissolve on warming. If the acid is impure, an excess of urates also causes a precipitate, but it redissolves on boiling the solution. In the latter case, a diabetic condition is indicated, and the presence of reducing sugars may be tested for by adding copper sulphate and an alkali hydroxide, or preferably, for the sake of convenience, a tablet containing 0.02 gram of copper sulphate and 0.01 gram each of sodium carbonate and calcium hydroxide. G. F. M.

**Volumetric Analysis of Ion-protein Compounds.** JACQUES LOEB (*Proc. Soc. Exp. Biol. Med.*, 1918, **16**, 39).—Gelatin at  $p_H > 4.7$  combines only with cations and at  $p_H < 4.7$  only with anions, whilst at the isoelectric point ( $p_H = 4.7$ ) it combines with neither anion nor cation. Curves representing the influence of univalent anions or cations on the swelling, osmotic pressure, and viscosity of gelatin are always approximately parallel with the curves representing the amount of anion or cation found in chemical combination with the gelatin. CHEMICAL ABSTRACTS.

**Estimation of Pepsin.** JOHN H. NORTHPROP (*J. Gen. Physiol.*, 1919, **2**, 113—120).—See this vol., i, 193.

**Influence of Acetic Acid on the Benzidine Reaction.** EMMO SCHLESINGER and JULIUS GATTNER (*Berl. Klin. Woch.*, 1919, **56**, 706—707; from *Chem. Zentr.*, 1919, iv, 526).—The discordant views of different authors on the value of the benzidine reaction in the detection of blood are due to the previously unnoticed fact that the sensitiveness of the reaction is a function of the concentration of the benzidine in the acetic acid. The authors find that a blue substance is the actual product of the benzidine reaction; this is precipitated if the proportion of acetic acid to benzidine is low, and is thus removed from further action and remains stable for a long period. In the presence of an excess of acetic acid, however, it dissolves, with the formation of a very unstable, green solution. Diagnostic conclusions cannot therefore be immediately based on the occurrence of one or other coloration, since the quantity of acetic acid used is a decisive factor. The blue colour invariably becomes green on addition of acetic acid. H. W.

**Reduced Eosin as a Reagent.** LUCIANO P. J. PALET and AMANCIO FERNANDEZ (*Anal. Soc. Quim. Argentina*, 1918, **5**, 119—120).—Traces of blood in dilute solution may be detected by means of the fluorescence produced with an alkaline solution of the leuco-derivative of eosin. The substitution of fluorescein for eosin is recommended. W. S. M.

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## General and Physical Chemistry.

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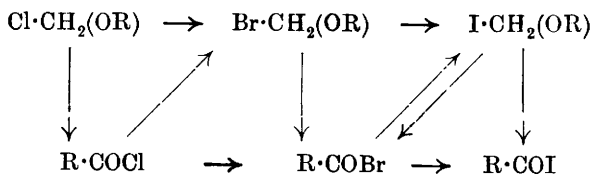
**The Optics of Disperse Systems. III.** I. LIFSCHITZ and GEORG BECK (*Kolloid Zeitsch.*, 1920, **26**, 10—15. Compare A., 1918, ii, 181, 253).—The authors have measured the refractive index of solutions of triethylamine, gelatin, and phenol in water and of silicic acid, stannic acid, arsenic sulphide, antimony sulphide, and vanadium pentoxide sols in water by the method previously described (*loc. cit.*). The measurements were made at a series of temperatures with the object of ascertaining the effect of change in the dispersity on the refractive index. It is shown that the degree of dispersion is practically without effect on the refractive index. In the cases of phenol and triethylamine, where on lowering the temperature beyond the critical solution temperature a separation of the two liquids occurs, there is only a very small change of refractive index shown. In the case of gelatin the value of the specific refraction varies very much with the temperature, whether calculated by the Gladstone and Dale formula or by the Lorenz and Lorentz formula. In all other cases the value is approximately constant when either formula is used, but the values given by the Gladstone and Dale formula are more nearly constant than the others. J. F. S.

**The Spectrochemical Behaviour of Halogen Ethers,  $\text{RO}[\text{CH}_2]_n\text{X}$ , Halogen Hydrins,  $\text{HO}[\text{CH}_2]_n\text{X}$ , and Acid Bromides,  $\text{R}\cdot\text{COBr}$ .** A. KARVONEN (*Acad. Sci. Fennicae*, 1914, A, **5**, 1—139; from *Chem. Zentr.*, 1919, iii, 807—808).—In continuation of previous work (A., 1913, i, 2) a series of halogen ethers and halogen hydrins has been refractometrically investigated. New values for the atomic refraction of chlorine, bromine, iodine, and oxygen have been deduced from observations on normal primary alkyl monohaloids and the mono-ethers of normal primary alcohols. The data obtained for chlorine and iodine agree excellently with Eisenlohr's figures; on the other hand, the new values for bromine and ethereal oxygen differ considerably from the older results. The following figures are quoted:

	$\text{H}_\alpha$ .	D.	$\text{H}_\beta^F$ .	$\text{H}_\gamma$ .	$\text{H}_\beta - \text{H}_\alpha$ .	$\text{H}_\gamma - \text{H}_\alpha$ .
$\text{Br}-\text{CH}_2-$ .....	8.688	8.748	8.888	9.010	0.199	0.318
$\text{O} \begin{Bmatrix} \text{CH}_2- \\ \text{CH}_2- \end{Bmatrix}$ .....	1.721	1.728	1.738	1.755	0.017	0.033

The  $\alpha$ -halogen ethers, particularly the iodo- and bromo-derivatives, show optical exaltations in the order  $\text{Cl}\cdot\text{CH}_2(\text{OR}) < \text{Br}\cdot\text{CH}_2(\text{OR}) < \text{I}\cdot\text{CH}_2(\text{OR})$ , whilst the behaviour of the  $\beta$ - and  $\gamma$ -halogen ethers and of the  $\beta$ - and  $\gamma$ -halogenhydrins is normal.

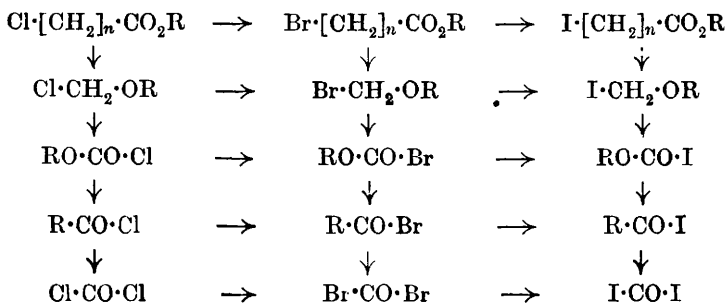
The acid bromides, like the corresponding chlorides, exhibit optical exaltation, the order being  $R \cdot COCl < R \cdot COBr < R \cdot COI$ . The atomic refraction of bromine in acid bromides is  $H_a$  9.514,  $D$  9.595,  $H_\beta$  9.805,  $H_\gamma$  9.987,  $H_\beta - H_a$  0.292,  $H_\gamma - H_a$  0.467. Among the compounds  $X \cdot CH_2(OR)$  and  $R \cdot CO \cdot X$  the optical exaltations increase in the direction of the arrows:



When substituents, such as the halogens alone or with oxygen or alkyl groups, accumulate around a carbon, nitrogen, or phosphorus atom, the optical exaltations fairly generally increase and the depression diminishes. The reverse behaviour is particularly noticeable when the atom adjacent to the central atom is attached to a number of substituents or is multiply linked. The accumulation of ethereal groups appears generally to have a depressing influence.

H. W.

**Influence of Position and Accumulation of Substituents on Spectrochemical Behaviour. II. The Spectrochemistry of Halogen and Oxygen Compounds.** A. KARVONEN (*Acad. Sci. Fennicae*, 1916, A, 10, No. 4, 1—22; from *Chem. Zentr.*, 1919, iii, 808. Compare preceding abstract).—The exaltation caused by the accumulation of chlorine and oxygen atoms has been confirmed by observations on a series of chlorinated aliphatic esters. In general, the optical exaltation diminishes when the halogen atoms in the chain are further removed from one another or from the oxygen atom. The esters of aliphatic acids containing a chlorine atom attached to the terminal carbon atom appear to exhibit a slight optical depression. In the annexed combinations, the optical exaltations increase in the direction of the arrows:



H. W.

**Influence of Position and Accumulation of Substituents on Spectrochemical Behaviour. III. Spectrochemical Behaviour of the Esters of Normal Acids of the Oxalic Series.**

A. KARVONEN (*Acad. Sci. Fennicae*, 1916, A, 10, No. 5, 1—20; from *Chem. Zentr.*, 1919, iii, 811. Compare preceding abstracts).—Optical investigation of the methyl and ethyl esters of the oxalic series shows that the exaltation diminishes uniformly as far as the succinic esters with increasing separation of the carboxyalkyl groups. The oxalic esters show slight exaltation, malonic esters behave normally, and the succeeding esters exhibit a slight depression with a tendency to increase in refraction towards the higher members. Esters of suberic and sebacic acids behave similarly to other esters of the oxalic series.

H. W.

**Influence of Position and Accumulation of Substituents on Spectrochemical Behaviour. IV. Spectrochemical Behaviour of Ether-Esters,  $\text{RO} \cdot [\text{CH}_2]_n \cdot \text{CO}_2\text{R}$ .**

A. KARVONEN (*Acad. Sci. Fennicae*, 1916, A, 10, No. 6, 1—14; from *Chem. Zentr.*, 1919, iii, 811. Compare preceding abstracts).—The following substances have been investigated: ethyl and methyl carbonates, methyl methoxyacetate, ethyl ethoxyacetate, propyl propoxyacetate, methyl  $\beta$ -methoxypropionate, ethyl  $\beta$ -ethoxypropionate, propyl  $\beta$ -propoxypropionate, methyl  $\alpha$ -methoxypropionate, and ethyl  $\alpha$ -ethoxypropionate. In the case of the lower fatty esters, the optical values diminish when a hydrogen atom of the acid radicle is replaced by an alkyloxy-group. The optical depressions diminish as the ethereal oxygen atom and the carbonyl group become more distantly separated in the alkyloxy-aliphatic esters.

H. W.

**Secondary Spectrum of Hydrogen.** T. R. MERTON (*Proc. Roy. Soc.*, 1920, [A], 96, 382—388).—The spectrum of hydrogen at 1 mm. pressure, and of hydrogen in helium at 40 mm. pressure have been photographed, using a concave grating 120 cm. radius of curvature and ruled 8000 lines per cm. It is shown that the lines of the secondary hydrogen spectrum in the red and yellow regions are greatly enhanced in the presence of helium, and that other new lines appear. In the more refrangible parts of the spectrum there is little difference in the intensity of the lines in the two cases. A second class of lines is not affected at all by the presence of helium, whilst a third class diminishes in intensity and in some cases disappears entirely. It is suggested that the change in intensity under the experimental conditions may serve as a method of investigation of the secondary hydrogen spectrum. Photographs of both spectra are given over the range  $\lambda$  4300— $\lambda$  6500. A tabulated list of the lines which are not affected and of those which are enhanced in the presence of helium together with the intensities under the two sets of conditions is appended to the paper. The lines  $\lambda$  5831.26 and 5703.86 are enhanced from intensity 2 to 7,  $\lambda$  5819.60 from 2 to 8, and  $\lambda$  5812.84 from 6 to 10.

J. F. S.

**Series of Multiple Lines in the Argon Spectrum.** KNUD. AAGE NISSEN (*Physikal. Zeitsch.*, 1920, **21**, 25—28).—A theoretical paper in which the lines of the argon spectrum are arranged into series.  
J. F. S.

**Spectra of Isotopes.** T. R. MERTON (*Proc. Roy. Soc.*, 1920, [A], **96**, 388—395).—The spectra of ordinary lead, lead from pitchblende and lead from thorite, ordinary thallium and thallium from pitchblende have been examined. An arc was produced between a tungsten button and the metal under investigation, in a bell jar at a pressure of 1 mm. The respective interference fringes produced by means of a Fabry and Perot étalon were photographed and measured by a micrometer. It is found that the line  $\lambda$  4058 in the case of pitchblende lead has a slightly greater wave-length than in the case of ordinary lead, whilst for lead from thorite, it is somewhat shorter. The measurements in the case of thallium are not conclusive because pure thallium was not isolated from pitchblende.  
J. F. S.

**A Relation between the Heads of Banded Spectra belonging to Different Elements of the same Group.** TOKIHARU OKAYA (*Proc. Phys. Math. Soc. Japan*, 1919, [3], **1**, 111—121).—It is shown that for the three elements gold, copper, and silver the wave-lengths of the heads of bands emitted by their molecules satisfy fairly well the linear relation  $\lambda = \alpha + \beta n$ , where  $\alpha$  and  $\beta$  are constants and  $n$  is the series of natural numbers. From this it is concluded that between the heads of the band spectra emitted by the different molecules in similar conditions there exists a simple relation when the bands diverge toward the red side. Thus, the wave-length  $\lambda$  of the head of some band of one element with reference to the corresponding one  $\lambda'$  of another element is given by the relation  $\lambda = (\alpha + \beta n)(m/m')^{\frac{1}{2}}(p/q)^{\frac{1}{2}}$ ,  $p$  and  $q$  being certain integers,  $m$  and  $m'$  the atomic weights of the elements concerned, and  $\lambda' = (\alpha + \beta n)$ .  
CHEMICAL ABSTRACTS.

**Spectra of Tin, Lead, Antimony, and Bismuth in a Magnetic Field.** P. A. VAN DER HARST (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 300—312).—Using the light from a condensed spark between poles of tin, lead, antimony, and bismuth respectively, the author has examined the effect of a magnetic field of about 30,000 gauss on a number of lines of these metals. The Zeeman effect is measured for 35 lines of tin, 23 of lead, 27 of antimony, and 16 of bismuth. The measurements show deviations from those previously published by Purvis (A., 1907, ii, 919), due to uncertainty in the strength of the field used by Purvis. The resolutions of the lines are fairly regularly distributed between values which are 1—1.5 times the normal resolution. Incidentally, it is shown that the antimony lines  $\lambda$  4370, 4295, 4287, 4091, 4078, 4038, 4024, 4006, 4004, 3979, 3721, 3467, and 3460 measured by Schippers (A., 1912, ii, 877), and published in Kayser's "Handbuch der Spectroscopie," do not exist. The lines are respectively

λλ 2913, 2863, 2858, 2727, 2719, 2692, 2683, 2671, 2670, 2653, 2480, 2311, and 2306. The error has arisen by Schippers mistaking lines of the third order for lines of the second order. J. F. S.

**Colour of Metallic Salts.** YUSI SHIBATA (*J. Tokyo Chem. Soc.*, 1919, **40**, 463—482).—From the spectral analysis of compounds of cobalt, nickel, and chromium the author deduces that the region of colour formation in these salts lies between the non-metallic atomic group and the metallic group which form a nucleus for the complex ions or double salts. In no case is colour developed by metallic salts without the formation of complex ions. Colourless complex inorganic salts which show strong absorption in the ultra-violet are composed of constituents which are absolutely transparent in this region. A theory is developed which leads to the conclusion that the wave-length of the light absorbed is longer the smaller is the atomic volume of the metal forming the centre of the complex. The conclusion is supported by experimental evidence in the case of correspondingly constituted complex salts of zinc, platinum, copper, tin, silver, cadmium, and mercury.

The application of the theory to chromophores in organic compounds is discussed.

CHEMICAL ABSTRACTS.

**Relation between the Visible Absorption Spectra of certain Metals in their  $M'^vX_4'$  and  $(M_2)^{vi}X_6'$  Derivatives.**

MATHEUS D'ANDRADE ALBUQUERQUE (*Revista Chim. pura applic.*, 1916, **1**, Reprint 14 pp.).—In order to verify the law of the conservation of even or odd valencies in derivatives of the same element, evidence was sought for the existence of molecules of the type  $M_2X_6'$  in salts derived from sesquioxides. A number of coloured salts with colourless anions were investigated in non-dissociating solvents, or compounds containing complexes, such as  $K_2MX_6$  and  $K_3MX_6$ . Two methods were available: (1) combination of two different salts of the type  $M_2X_6$  so as to obtain a mixed salt  $MM'X_6$ ; if the properties of the latter were different from those of  $M_2X_6$  and  $(M')_2X_6$ , the difference must be attributed to linking between M and M'; (2) spectrographic evidence for some union between M and M'. The observation of the absorption spectra proved that the normal salts derived from sesquioxides always presented absorption bands, most of which were in the region where salts of the type  $MX_4$  of the same element show no absorption. When an element combines with another in different proportions, the colour of the compounds shifts towards the red end of the spectrum as the valency increases; and as the colour of sesquioxide salts is often abnormal, this must be attributed to a radicle which can only be  $M_2$ . In the iridichlorides of silver and thallium the author assumes the presence of a complex radicle containing iridium because, unlike other reddish-brown iridichlorides, the salts are blue and bluish-green respectively, that is, approximating towards the colour of  $IrCl_3$  or  $Ir_2Cl_6$ . It is observed that didymium gives a characteristic absorption spectrum differing from those of praseodymium and neodymium.

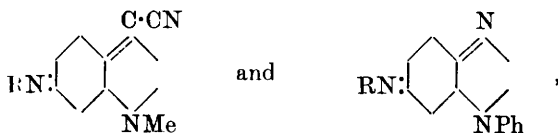
ium, which points to the existence of an atomic complex. In the majority of cases the colour of salts of the type  $M_2X_6$  is complementary to that of the salts  $MX_4$  of the same element, a property which will be discussed in a future paper.

W. R. S.

**Absorption Bands in the Ultra-violet and Magnetic Birefracton.** GUSTAVE MASSOL and A. FAUCON (*Bull. Soc. chim.*, 1919, [iv], **25**, 585—588).—It is shown that the substances or groups which give absorption bands in the ultra-violet also exhibit magnetic birefracton as found by Cotton and Mouton (compare A., 1910, ii, 368).

W. G.

**Quinone-imide Dyes. XII. Absorption Spectra of some Cyanoacridine and Cyanopyronine Dyes.** F. KEHRMANN and M. SANDOZ (*Ber.*, 1920, **53**, [B], 63—66).—In an earlier paper (A., 1918, i, 313) it was shown that the substitution of the group :C:C:N for the tervalent nitrogen atom in safranines and azoxines has practically no effect on the colour. The absorption spectra for three sets of comparable dyes have now been determined, revealing the same feature. In fact, the groups



especially may be regarded as optically equivalent.

J. C. W.

**Determination of the Constitution of Coloured Substances from their Absorption Spectra. II.** F. KEHRMANN and MAURICE SANDOZ (*Helv. Chim. Acta*, 1920, **3**, 104—114. Compare A., 1918, ii, 418).—The absorption spectra of the mono- and di-amino- and of the dianilino-phenazines have been examined.

Alcoholic solutions of phenazine and aminophenazine are almost colourless and orange respectively, whilst similar solutions of *s*- and 2:3-diaminophenazines are pale yellow and very light yellow; this is in accordance with the authors' theory that the introduction of an amino-group in the para-position to the nitrogen of quinone-imines or in the same position with respect to the carbon atom of triphenylmethane has a hypsochromic or bathochromic influence which depends on the basicity of the group into which it enters. The introduction of the first amino-group into phenazine considerably increases the basicity, but this is not the case with the second group. Phenylated derivatives of phenazine are slightly more red than the corresponding non-phenylated compounds, but are chiefly noticeable for the augmentation of the intensity of colour effected by introduction of the phenyl group. In general, the absorption curves of the bases do not present any striking anomalies, and the authors therefore attribute to them the orthoquinonoid structure of phenazine itself.



Mono- and di-aminophenazines have very similar absorption spectra when dissolved in fuming sulphuric acid, which closely resemble that of the di-acid salt of phenazine; they appear, therefore, to have the orthoquinonoid structure, the imino-groups having lost their auxochromic effect by conversion into amino-salts. When, however, the solutions are gradually diluted with concentrated sulphuric acid, the blood-red colour suddenly changes to green, the shade differing somewhat with the individual compound. The gradual dilution of the acid appears to cause hydrolysis of the poly-acid salts and to liberate one by one the auxochrome groups, the activity of which has been paralysed by salt-formation. Thus the green shade of the tri-acid salt of diaminophenazine gradually gives place to the violet tint of the di-acid salt and to the cherry coloration of the mono-acid salt. Since the successive transformations take place in a continuous manner without appearance of any striking anomalies, the authors ascribe the paraquinonoid constitution to the di-acid and mono-acid salts, as well as to the green tri-acid compounds.

The ultra-violet spectra of the bases and of the mono-acid salts have been examined. With the former, an absorption band is invariably observed, which becomes progressively displaced towards the visible violet as the chromogen becomes more highly substituted; it is situated at  $\lambda = 250 \mu\mu$  for phenazine, at  $\lambda = 265 \mu\mu$  for the mono- and di-aminophenazines, and at  $\lambda = 285 \mu\mu$  for dianilinophenazines. The position of the anilino-groups which has such a marked influence on the position of the bands in the visible spectrum appears to have no effect on the location of the band in the ultra-violet. The mono-acid salt of aminophenazine gives two bands in the ultra-violet, that of 1:2-diaminophenazine has one band in the visible violet ( $\lambda = 457 \mu\mu$ ), whilst the second is but slightly shifted; that of *s*-diaminophenazine shows only one band in the ultra-violet, the second having completely disappeared. The mono-acid salts of the anilinophenazines likewise only show one band in the ultra-violet ( $\lambda = 285 \mu\mu$ ). It appears, therefore, that isomeric substances with equal molecular weights give superposable spectra in the ultra-violet.

H. W.

**Photochemical Actions produced in Crystals by means of Polarised Light.** M. PADOA (*Atti R. Accad. Lincei*, 1919, [v], 28, ii, 372—377).—The author has studied the action of polarised light on crystals of cinnamic acid, *o*-nitrobenzaldehyde, and cinnamylidenemalononic acid (compare Weigert, A., 1918, ii, 344), all of which compounds undergo pronounced photochemical transformations.

After exposure to the action of light, crystals of cinnamic acid become dulled, the dimeric  $\alpha$ -truxillic acid being formed (compare Stobbe, A., 1919, i, 329). Since this action is manifest only after prolonged exposure, it may be assumed that solid solutions between the monomeric and dimeric forms are first formed; that such solutions are supersaturated is confirmed by the normal cryoscopic

behaviour of  $\alpha$ -truxillic acid in cinnamic acid solution, and melting-point measurements indicate the concentration limit of the supersaturated solutions to be 3% of the truxillic acid. No appreciably different results were obtained on exposing crystals of cinnamic acid to the action of polarised light, in the one case with the plane of polarisation parallel, and in the other normal, to one pair of parallel edges of the crystal.

When two prismatic crystals of *o*-nitrobenzaldehyde (compare Lobry de Bruyn and Jungius, A., 1903, ii, 531; Bruni and Callegari, A., 1904, ii, 545) are crossed normally and exposed in a polarising microscope to the influence of polarised light with the plane of polarisation at  $45^\circ$  to the axes of the two crystals, one of the latter undergoes change more rapidly than the other.

Results similar to, but more pronounced than, those obtained with *o*-nitrobenzaldehyde are observed in the case of cinnamylidenemalononic acid. After an exposure to the action of polarised light varying, according to the magnitude of the crystals, from one and three-quarters to three hours, part of the crystal, with its axis perpendicular to the plane of polarisation, is violently detached and often projected to a distance; in some cases, however, only transverse segmentations appear in the crystals, such occurring earlier and in greater number in the crystal mentioned. Subsequently, crystalline nodules of the dimeride make their appearance. Here too it may be assumed that solid solutions of the dimeride in the monomeride are first formed, these solutions being so unstable as to produce a condition of tension in the crystals, and consequent explosion. The partial transformation of the monomeride into the dimeride may be followed by means of the melting point, which shows marked lowering even before any change in the crystal is apparent.

Weigert's conclusions are criticised, and arguments are advanced in support of the view that phototropy is to be classed among the real photochemical phenomena.

T. H. P.

**Behaviour of Fehling's Solution in Light.** IVAN BOLIN and GUNNAR LINDER (*Zeitsch. physikal. Chem.*, 1919, **93**, 721—736).—The action of light from a carbon arc on Fehling's solution in glass and quartz vessels has been studied at  $15^\circ$  and  $25^\circ$ . The amount of cuprous oxide precipitated was estimated by titration with potassium permanganate. The light reactions were compared with the reactions occurring in the dark. It is shown that in glass vessels the reaction has no temperature-coefficient, and that there is no evolution of gas. The velocity of reaction is proportional to the time during which the solution has been illuminated, and on removing the light the reaction ceases. In quartz vessels, the reaction has a temperature-coefficient 1.2, and after about three hours' illumination there is an evolution of gas. The velocity of the reaction increases with the time of illumination, and when the light is removed, the reaction continues for some time. The difference in the course of the reaction in glass and quartz vessels is explained

as follows. In quartz vessels, in addition to the photochemical reaction, an ordinary chemical reaction also takes place. This reaction is caused by substances produced in the photo-reaction. Both reactions produce cuprous oxide, the chemical reaction increasingly more as reducing substances are produced photochemically. Consequently, the total amount of cuprous oxide produced increases progressively with the time. On shutting off the light, the reaction continues until all the reducing substances have been used up. The reaction is more pronounced in quartz vessels, because these allow light of smaller wave-length than  $350\text{ }\mu\mu$  to enter the liquid, and it is due to these waves that the reducing substances are produced from the tartrate in the solution. J. F. S.

**The Recoil of  $\alpha$ -Particles from Light Atoms.** L. B. LOEB (*Phil. Mag.*, 1919, [vi], **38**, 533—541).—An account is given of an attempt to verify the conclusion of Rutherford, namely, that in collisions between  $\alpha$ -particles and light atoms, the number of atoms projected straight forward within an angle of  $10^\circ$  from that of the  $\alpha$ -particle is ten to thirty times that calculated from Darwin's theory of point charges, by examining the number of  $\alpha$ -particles recoiling after collision with light atoms. The conditions necessary to ensure success and overcome the numerous difficulties are worked out, but the results are provisional and indecisive for lack of sufficient time. They indicate that for aluminium the abnormalities found by Rutherford for nitrogen and hydrogen begin to show themselves, but the experimental difficulties were not overcome for lighter elements, such as carbon. The range of the  $\alpha$ -particle deflected at  $105^\circ$  from aluminium was found to be below  $3.6\text{ cm.}$ , as is to be expected if the laws of energy and momentum apply to these close encounters. F. S.

**Passage of Corpuscular Rays through Material and the Constitution of the Atom.** I. R. SEELIGER (*Jahrb. Radioaktiv. Elektronik*, 1919, **16**, 19—65).—A theoretical paper in which the author discusses the work of many investigators on the passage of  $\alpha$ - and  $\beta$ -rays through material. The consideration is concerned with the individual processes and changes brought about by the passage of a corpuscular ray through an atom or a molecule. These changes are subdivided into changes in the moving particle: (i) direct conveyance of kinetic energy to the atom, and (ii) emission of electromagnetic radiation; and into changes in the atom: (i) direct gain in kinetic energy, (ii) emission of electromagnetic radiation, (iii) emission of secondary corpuscular radiation, and (iv) chemical changes. J. F. S.

**Connexion between Collision Ionisation and the Energy of Ionisation of Neutral Molecules.** J. FRANCK, P. KNIPPING, and THEA KRÜGER (*Ber. Deut. physikal. Ges.*, 1919, **21**, 728—732).—The ionisation steps of hydrogen have been investigated. It is shown that definite ionisation occurs at  $11.5 \pm 0.7$  volts,  $17.1 \pm 0.25$

volts, and  $30.4 \pm 0.5$  volts. The first step corresponds with the formation of  $H_2^+$ , and the measurements show that an ion with considerably larger diameter is formed at 11.5 volts than at 17 or 30 volts. At  $13.6 \pm 0.7$  volts there is an emission of ultra-violet light, the potential  $17.1 \pm 0.25$  volts corresponds with the ionisation of the atom into a normal, and a positive ion and an electron, and the potential  $30.4 \pm 0.5$  volts corresponds with ionisation of the atom into two positive ions and two electrons. These results go to show that the Bohr atom model of hydrogen is not strictly in keeping with the facts. J. F. S.

**Apparatus for the Separation of Radium Emanation and its Estimation Electroscopically.** J. E. UNDERWOOD and HERMAN SCHLUNDT (*Trans. Amer. Electrochem. Soc.*, 1918, **34**, 203—209).—An apparatus is described by means of which radium in various ores and concentrates may be estimated. The material is either boiled with concentrated sulphuric acid or fused with a mixture of alkali carbonates or with sodium hydrogen sulphate in one part of the apparatus, and the emanation stored in a mercury burette in another part of the apparatus. The emanation is kept for ten minutes in the burette to allow the thorium emanation to decay, and is then passed into the electroscope, where it is measured in the usual way. Using this method, Brazilian monazite is shown to contain  $0.794-0.812 \times 10^{-7}$  gram radium per gram; Indian monazite,  $0.1017-0.1025 \times 10^{-7}$  gram radium per gram. J. F. S.

**Comparison of the Ionisation Currents due to Equal Quantities of Radium Emanation in Different Types of Electroscopes.** T. H. LEAMING, HERMAN SCHLUNDT, and JULIUS E. UNDERWOOD (*Trans. Amer. Electrochem. Soc.*, 1916, **30**, 365—378).—The authors have compared the ionisation currents obtained with several types of electroscopes (Lind, Wulf quartz fibre, Fontactometer, Duane and Laborde, and Randall), and find that, with the exception of the Randall rectangular electroscope, the measured currents have lower values than the values calculated by the formula of Duane and Laborde,  $I = K(I - C.S/V)$ . In some cases, the values were 18—22% too low. The experiments show that the reduction factor,  $C$ , of Duane and Laborde's formula has specific values for ionisation chambers of definite dimensions. J. F. S.

**Absorption of Radium Gamma Rays.** K. W. F. KOHLRAUSCH (*Sitzungsber. K. Akad. Wiss. Wien*, 1917, **126**, IIa, 683—704).—The results of the investigation are given in the following table, where  $K_1$ ,  $K_2$ , and  $K_3$  are the three components of the complex  $\gamma$ -rays from radium:

*Absorption Coefficients  $\mu_1$ ,  $\mu_2$ , and  $\mu_3$ .*

Absorber.	$K_1$ .	$K_2$ .	$K_3$ .
Lead .....	0.545	1.4	4.6
Zinc .....	0.327	0.57	1.44
Iron .....	0.356	0.63	3.00
Aluminium .....	0.127	0.23	0.57

The ratio of the energies measured by ionisation currents is, for these three components,  $K_3:K_2:K_1=1:6:8$ . The absorption measurements show that the influence of secondary radiation is extremely important.

CHEMICAL ABSTRACTS.

**The Hard Secondary Gamma Rays from Radium.** K. W. F. KOHLRAUSCH (*Sitzungsber. K. Akad. Wiss. Wien*, 1917, **126**, IIa, 705—720).—In a previous paper (compare preceding abstract) the author made a careful series of measurements of the absorption of the  $\gamma$ -rays of radium in various substances. In these experiments, the importance of secondary radiation was indicated. The present paper deals with this secondary radiation, which is shown to have a high penetrating power. When the  $\gamma$ -rays pass through matter, a very hard type of secondary radiation ( $\mu_{Pb}=0.545 \text{ cm.}^{-1}$ ) is produced. The author compares the observed total energy of the secondary radiation with the calculated values for varying thickness of screen. The observations are in good agreement with theory.

CHEMICAL ABSTRACTS.

**Absorption of Gamma Rays from Radium.** K. W. F. KOHLRAUSCH (*Sitzungsber. K. Akad. Wiss. Wien*, 1917, **126**, IIa, 887—913).—The results are given of an extensive series of measurements of the absorption coefficients of radium  $\gamma$ -rays in different substances.

CHEMICAL ABSTRACTS.

**The Chemical Character of Protoactinium [Ekatan-talum]. I. Separation of Protoactinium from Pitchblende.**

OTTO HAHN and LISE MEITNER (*Ber.*, 1919, [B], **52**, 1812—1828).—The raw material for the preparation of protoactinium is the insoluble residue, consisting principally of silica, from pitchblende after treatment of the mineral with nitric acid. By repeated extraction with nitric acid, all the radioactive substances, including radium, can be dissolved, and the residue left with a very feeble  $\alpha$ -activity, due chiefly to protoactinium. It is recommended to add from  $\frac{1}{2}\%$  to 1% of tantalum oxide to the pitchblende residue and to heat it with a little concentrated sulphuric acid and excess of 40% hydrofluoric acid in a platinum capsule covered with a platinum dish containing cold water to serve as a condenser, then to dilute and filter through a paraffined funnel, evaporate the filtrate, and ignite the residue gently, which renders the tantalum oxide containing the protoactinium insoluble in acids. An addition of a few milligrams of thorium and of lead nitrates to the hydrofluoric acid serves to keep traces of ionium, uranium-X, and radio-lead from passing through the filter with the tantalum. The ignited tantalum oxide is boiled with aqua regia to remove iron, zirconium, etc., leaving the tantalum undissolved.

The Rutherford-Boltwood ratio of 8% for the actinium branch series would, neglecting correction for difference of range, lead to an  $\alpha$ -activity of proto-actinium 4% of that of the uranium in the mineral from which it is extracted. This is found to be much too high. The protoactinium was separated from known amounts of

pitchblende by three different methods, detailed below, and the  $\alpha$ -activity of the preparation extracted per gram of mineral was found to be the same, within 10%, in six experiments, from which, after applying a correction for the range, it is calculated that only 3% of the atoms of uranium disintegrating pass through the protoactinium, actinium series. The three methods consist of: (1) fusion of the pitchblende with sodium hydrogen sulphate, followed by treatment of the insoluble residue with hydrofluoric acid, as already detailed; (2) treatment of the very finely divided mineral with hydrofluoric acid and sulphuric acid, in which the main part of the protoactinium passes into solution directly; (3) treatment of the mineral very similarly to that described already for the residue. Full details of the chemical operations and charts are given showing, in each case, the distribution of the radio-elements in the successive stages of treatment. Tantalum oxide was always added to the mineral, and elaborate care taken, more of this material being added and separated from each of the separate parts to remove protoactinium, to ensure that all was separated. Finally, as a test, a known amount of previously prepared protoactinium preparation was added to pitchblende, and the result showed that no loss, exceeding 5%, occurred in the course of the chemical treatment.

The low percentage of the actinium series operates against sufficient protoactinium being present in uranium minerals for isolation like radium. Its period of average life can only be fixed within the limits of 1200 and 180,000 years at present, which correspond with weights in the mineral of 1.5% and 22.5% of the weight of contained radium. So far, efforts to concentrate it from tantalum have failed. It is suggested that an examination of the amount of protoactinium in old uranium preparations might throw further light on the period, and uranium preparations of known age of uranium, not less than 100 to 200 grams, are appealed for. The 3% ratio agrees with the ratio found for the relative activities of uranium- $X_1$  and uranium- $Y$ . It is pointed out that protoactinium with atomic weight about 230 and place in the periodic table beyond thorium, of atomic weight 232, furnishes probably another example similar to that of tellurium and iodine. F. S.

**The Origin of Actinium.** OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1919, 20, 529—533. Compare preceding abstract).—The paper contains some further details of the methods employed for determining the relative  $\alpha$ -activity of the preparations measured. F. S.

**Determination of the Half-life Periods of Thorium and Actinium Emanations.** R. SCHMID (*Sitzungsber. K. Akad. Wiss. Wien*, 1917, 126, IIa, 1065—1079).—The author describes a method which is the same in principle as that used by Leslie and Perkins. Measurements were also made by Rutherford's method, in which the ionisation current is measured at different points along a tube

through which the emanation is flowing at a known rate. A third method employed is due to Mache. The mean results of the investigation are as follows: half-life period for thorium emanation  $54.5 \pm 0.03$  secs.; for actinium emanation  $3.92 \pm 0.015$  secs.

CHEMICAL ABSTRACTS.

**The Age of Thorium Minerals.** R. W. LAWSON (*Sitzungsber. K. Akad. Wiss. Wien*, 1917, **126**, IIa, 721—739).—The paper deals with the end-product of the thorium series in the light of the atomic weight results of Hönigschmid and others. It is shown that the age, determined from the Th/U and Pb/U ratios, may be between 8 and 300 million years. The minerals employed came from Devon, Brevig, and Norway. The possible origin of the large discrepancy in age is discussed. Thorium minerals from Ceylon give a range from 138 to 506 million years.

CHEMICAL ABSTRACTS.

**Electrolytic Dissociation Theory.** GEORGE SENTER (*Trans. Faraday Soc.*, 1919, **15**, 3—9).—An introductory paper to a discussion of *The Present Position of the Theory of Ionisation* (see following abstracts), in which the author summarises certain investigations on electrolytes in solution, namely, hydration, deviation of strong electrolytes from the law of mass action, and the chemical activity of ions and non-ionised molecules. It may be regarded as established that ions and undissociated molecules may simultaneously undergo chemical change, and that in the catalytic activity of strong acids the non-ionised molecule plays a part as well as the hydrogen ion.

J. R. P.

**Electrolytic Dissociation.** SVANTE ARRHENIUS (*Trans. Faraday Soc.*, 1919, **15**, 10—17).—The author summarises the present evidence in favour of the dissociation theory of solution under eleven headings: (1) Evidence from analytical chemistry. (2) Additive properties. (3) The diffusion of electrolytes. (4) The electric conductivity of solutions. (5) Colours of solutions. (6) Ostwald's law. (7) Non-aqueous solutions. (8) Ostwald's law for salt solutions in water. (9) The freezing point of aqueous solutions. (10) Deviations in concentrated solutions. (11) Velocity of reaction.

J. R. P.

**Present Position of the Ionisation Theory: Reactions of both the Ions and Molecules of Acids, Salts, and Bases.** S. F. ACREE (*Trans. Faraday Soc.*, 1919, **15**, 18—26).—Mainly an historical account of attempts to elucidate the so-called "abnormal salt effect" of dissolved electrolytes. Results on the inversion of sucrose and other reaction velocities are explained by assuming that molecules, as well as ions, are active. The acid molecules are found to be two or three times more active than the hydrion in the case of hydrochloric, hydrobromic, and nitric acids, as measured by the hydrolysis of sucrose. A similar conclusion was reached for the hydrolytic activity of alkalis. The activity of molecules is also deduced from a study of the action of alkyl haloids in alcoholic

solution on phenoxides. Another cause of abnormal salt effect is solvation, studied by Lapworth. Several tables of values of the velocity constants of ions and molecules, deduced from the author's results and from re-interpretation of those of other workers, are given.

J. R. P.

**The Bearing of Migration Data on Conduction in Solutions. The Electrochemistry of Sodium Iodide in Acetone.**

JAMES W. MCBAIN and F. C. COLEMAN (*Trans. Faraday Soc.*, 1919, 15, 27—46).—When the sum of the movements of both ions is equal to the total current, the solvent cannot be appreciably dissociated. This is the case in aqueous solutions. Hypotheses to the contrary are therefore invalidated. The migration data for solutions of sodium iodide in acetone, and of silver bromate in diethylamine, show that, even in highly concentrated solutions, the solvent does not conduct appreciably. The evidence of the migration data shows that conductivity is only an approximate measure of the degree of dissociation, since the migration ratio almost invariably increases with the concentration, a change ascribed to solvation. The calculation of conductivities at infinite dilution from extrapolation of dilution formulæ to infinite dilution, or from the assumption of the law of mass action at infinite dilution, are regarded with disfavour. The molecular weight of sodium iodide in acetone, determined by the boiling-point method, is normal.

J. R. P.

**The Determination of the Ionisation of an Aqueous Solution.**

W. R. BOUSFIELD (*Trans. Faraday Soc.*, 1919, 15, 47—73).—A summary of the methods used by the author in calculating the ionisation of an electrolyte in aqueous solutions. Ionisation is assumed to be the result of the interaction of associated water molecules with the molecules of the salt, whereby  $(\text{H}_2\text{O})_3$  and  $\text{H}_2\text{O}$  molecules react with the salt to produce  $(\text{H}_2\text{O})_2$  molecules and hydrated ions. The application of the law of mass action then gives equations which give good results for a large class of strong electrolytes at high dilutions, and in the case of the alkali chlorides give good results in concentrated solutions. On account of varying hydration, it is assumed that the transport numbers require correction. This, however, cannot at present be carried out except by the method of trial and error. Stress is laid on the part played by the solvent, which is assumed to exist in associated forms, the proportions of which vary with the concentration of the solution.

J. R. P.

**Correction of the Transference Numbers of the Ions of an Electrolyte.**

W. R. BOUSFIELD (*Trans. Faraday Soc.*, 1919, 15, 74—80).—On the assumption that the volumes of the ions in solution are unequal, the correction necessary in the ordinary method of calculating the relative ionic mobilities from the transport numbers is found. The corrections are inappreciable at concentrations less than normal.

J. R. P.



**Some Aspects of the Electrolytic Dissociation Theory.**

NILRATAN DHAR (*Trans. Faraday Soc.*, 1919, **15**, 81—93).—By a discussion of recent work on electrolytes, including molecular-weight determinations, Kohlrausch's rule, freezing points, osmotic pressures, heats of neutralisation of acids and bases, and absorption spectra, the conclusion is drawn that the theory of non-ionisation proposed by Snethlage (*A.*, 1915, ii, 615, 825) is not tenable.

J. R. P.

**The Hydration of Ions.** HENRY J. S. SAND (*Trans. Faraday*

*Soc.*, 1919, **15**, 94—97).—In his calculations of the radii of ions, Bousfield adopts a radius for the water molecule which leads to a value for Avogadro's constant over twenty times that adopted in the same calculations. The values for the ionic radii deduced from Stokes's law do not agree with those derived from other calculations. It is believed that it is incorrect to apply the law of Stokes to molecular magnitudes.

J. R. P.

**Some Recent Investigations on the Dilution Law.** J. R.

PARTINGTON (*Trans. Faraday Soc.*, 1919, **15**, 98—121).—In the case of weak electrolytes the law of mass action applies with greater accuracy than to any other case yet investigated. The viscosity correction has been applied in a very arbitrary manner by many investigators, and the author believes that in dilute solutions it is unnecessary. The equation deduced by Szyskowski (*A.*, 1915, ii, 616) gives very accurate results for strong electrolytes, and renders unnecessary the arbitrary alterations made by Kraus and Bray (*A.*, 1913, ii, 914) in the accurate experimental values of Kohlrausch and Maltby (*A.*, 1900, ii, 61). It is shown that the theory proposed by Ghosh (*A.*, 1918, ii, 348, 392, 423) is not in accordance with the experimental results of the latter observers, since it requires equal ionisations at equal dilutions for all electrolytes of the same type, whereas differences are found. It is concluded that the law of mass action applies to strong electrolytes at great dilution.

J. R. P.

**Variation of Electrical Conductivity of Electrolytes with Increase of Concentration.** ALFRED W. PORTER (*Trans.*

*Faraday Soc.*, 1919, **15**, 122—125).—The empirical equation of Kohlrausch,  $1 - \alpha = \text{const.} \times c^{\frac{1}{2}}$ , is shown by a graphical method to hold over a large range. The index  $n$  of Storch's equation,  $\alpha/(1 - \alpha)^n = KV^{1-n}$ , is practically the same for potassium chloride as for sodium sulphate, in spite of the difference in valency. This equation has the form required by the law of mass action for a possible reaction, although the particular reaction which makes  $n = \frac{2}{3}$  (van't Hoff) has not yet been identified. The assumption of electrical action between the ions would lead to diminution of the ionisation  $\alpha$  with concentration at a greater rate than required by the law of mass action, whereas the opposite effect is actually found. If the law of mass action holds good at great dilution, it is necessary to explain the transition from this to the other laws which hold

at increased concentrations. A possible equation is  $\alpha^2(1 + b\alpha/V)/(1 - \alpha)[1 + c(1 - \alpha)/V] = \text{const.}$ , where  $b$  and  $c$  are additional constants.

J. R. P.

**The Resistance of an Electrolytic Cell.** EDGAR NEWBERY (*Trans. Faraday Soc.*, 1919, **15**, 126—136).—That part of the irreversible resistance of an electrolytic cell which is concerned in the transfer of the current from electrode to electrolyte has been studied in a number of cells. Transfer resistance is greatest when gases are liberated at the electrodes, considerable when gaseous ions are utilised in carrying the current, although not liberated at the electrodes, and negligibly small when the current is carried by metallic cations and by anions which readily dissolve the anode. Conditions favourable for high transfer resistance are low current density, low temperature, polished surfaces, and high over-voltages. Those conditions which affect the nature of the surfaces affect also the transfer resistance. Transfer resistance is due to the mechanical resistance (pressure and frictional) which opposes the penetration of gaseous ions into the surface of the electrodes. Measurements of electrical conductivity are liable to serious error if transfer resistance is not perfectly eliminated, and there is reason to fear that this has not been done in determining some of the conductivity data at present available.

J. R. P.

**Effect of Interionic Forces in Electrolytes.** S. R. MILNER (*Trans. Faraday Soc.*, 1919, **15**, 148—151).—Chemical forces, which cause the association of two ions into a molecule, diminish extremely rapidly with the distance, and become negligible at very small separations of the ions, whereas electrical forces between the ions fall off comparatively slowly. The ordinary derivation of the law of mass action for electrolytes assumes that interionic forces become negligible for finite separations of the ions. These forces, however, would cause a reduction of osmotic pressure and of molecular lowering of freezing point. The application of the inverse square law leads to general agreement with the observed freezing-point curves. The conductivity should be proportional to the osmotic pressure of the free ions, that is, those possessing sufficient kinetic energy to escape from their attracting neighbours.

J. R. P.

**Ionisation and the Mass Law.** H. M. DAWSON (*Trans. Faraday Soc.*, 1919, **15**, 152—153).—The deviations from the law of mass action in the case of strong electrolytes are ascribed mainly to changes in the ionising power of the solvent by the highly polar solutes.

J. R. P.

**The Abnormality of Strong Electrolytes.** JNANENDRA CHANDRA GHOSH (*Trans. Faraday Soc.*, 1919, **15**, 154—163).—The author does not agree with the criticisms of Partington (see above). The deviation from his theory shown by some electrolytes is ascribed to hydration of the ions.

J. R. P.

**Equilibrium between Bromine and Potassium Bromide Solutions at 0°.** GRINNELL JONES and MINER LOUIS HARTMANN (*Trans. Amer. Electrochem. Soc.*, 1916, **30**, 295—326).—Measurements of the equilibrium between bromine and water and between bromine and potassium bromide solutions at 0°, and of the specific conductivity of the solutions have been made. Calculations by the method of successive approximations based on the results show that the following reactions occur: (i) bromine dissolves as  $\text{Br}_2$ ; (ii)  $\text{Br}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}' + \text{Br}' + \text{HBrO}$ ; (iii)  $\text{KBr} + \text{Br}_2 \rightleftharpoons \text{KBr}_3$ ; (iv)  $\text{KBr} + 2\text{Br}_2 \rightleftharpoons \text{KBr}_5$ . A saturated solution of bromine in water at 0° has the composition  $\text{Br}_2 = 0.2539$  mol. per litre;  $\text{H}'$ , 0.001085;  $\text{Br}'$ , 0.000126;  $\text{Br}_3'$ , 0.000628; and  $\text{Br}_5'$ , 0.000331. The hydrolysis constant,  $K_H = (\text{H}')(\text{Br}')(\text{HBrO})/\text{Br}_2 = 5.7 \times 10^{-10}$ , the equilibrium constant,  $K_3 = \text{Br}' \times \text{Br}_2/\text{Br}_3' = 0.051$ ; and the equilibrium constant,  $K_5 = \text{Br}' \times \text{Br}_2^2/\text{Br}_5' = 0.0246$ . The partition-coefficient of  $\text{Br}_2$  between water and carbon tetrachloride after correcting for hydrolysis is  $D = 21.018 + 2.831C$ , where  $C$  is the concentration of  $\text{Br}_2$  in the carbon tetrachloride. By means of these constants the concentration of each ion may be calculated in any solution containing known amounts of potassium bromide up to 0.1*N* and bromine up to saturation. The conductivity of a series of solutions of potassium bromide from 0.001*N* to 0.1*N* has been determined at 0°. When extrapolated to infinity by Noyes' method, these results give 83.8 for  $\Delta_\infty$ , and if the ionic conductivity of  $\text{K}'$  is 40.1,  $\text{Br}'$  has the value 43.7. From the data for the specific conductivity of solutions of potassium bromide containing bromine it follows that the ionic conductivity of  $\text{Br}_3'$  is 23.5 and of  $\text{Br}_5'$ , 16.3. J. F. S.

**Corrosion of Metals by Acids.** OLIVER P. WATTS and NEWTON D. WHIPPLE (*Trans. Amer. Electrochem. Soc.*, 1917, **32**, 257—284).—The rate of corrosion and solution of iron, zinc, zinc amalgam, mercury, cadmium, tin, lead, copper, gold, silver, tin amalgam, and lead amalgam by means of hydrochloric acid, sulphuric acid, perchloric acid, phosphoric acid, and acetic acid, and also by solution of sodium hydroxide and a series of salts, has been determined. The effect of a number of oxidising agents on the rate of solution has also been investigated. The following oxidising agents were used: hydrogen peroxide, sodium arsenate, ferric sulphate, ferric chloride, potassium dichromate, potassium chlorate, mercuric chloride, potassium permanganate, potassium nitrate, chromic anhydride, nitric acid, potassium bromide, sodium nitrite, and potassium iodide. The authors confirm the view previously put forward (*ibid.*, 1912, **21**, 340) that the protective effect of arsenic on the corrosion of iron by sulphuric acid is due to polarisation by hydrogen. This view is confirmed by the facts that the corrosion of iron by acids when the metal was protected by arsenic was greatly accelerated by oxidising agents and arsenic does not protect iron from attack by corrosive agents which do not evolve hydrogen by their action. Amalgamation protects zinc from corrosion by acids because the discharge potential of hydrogen on mercury exceeds the potential on zinc. Protection by arsenic and mercury are alike in their

nature. Tin and lead are very slowly dissolved by non-oxidising acids, although their potentials are such as would cause their ready solution in acids, if it were not for the unusually high discharge potential of hydrogen on them. Removal of hydrogen by an oxidising agent causes these metals to dissolve readily in acids that otherwise corrode them very slightly. Corrosion by acids, of metals below hydrogen in the electrochemical series, namely, copper and silver, has been brought about by the presence of oxidising agents. The statement that the corrosion of amalgamated zinc in dilute sulphuric acid is accelerated in a vacuum is shown to be incorrect. By removing the depolarising oxygen of the air, reduction of pressure retards corrosion, not only of amalgamated zinc, but of other metals the solution of which is hindered by a polarising film of hydrogen. With respect to their corrosion the metals examined may be classified as follows: (a) Metals the potentials of which exceed the discharge potential of hydrogen on them; these dissolve readily in acids except such as form insoluble salts. (b) Metals the potentials of which are less than the discharge potential of hydrogen on them; these dissolve readily in acids only in the presence of oxidising agents. Gold and platinum are not readily attacked by acids in general, even when these contain oxidising agents. The superiority of nitric acid over other acids as a solvent for metals is due to its being at the same time an acid and an oxidising agent, which enables it to dissolve metals of the second class, which non-oxidising acids are unable to do. Oxygen is necessary for success in cyaniding gold ores because in dilute cyanide solutions gold is a metal of the second class. Measurements of the discharge potential of hydrogen in solutions of potassium cyanide and sodium hydroxide, and experiments on the corrosion of metals in the latter, lead to the conclusion that the above classification, the action of oxidising agents, and protection by other metals will apply to the dissolving of any metal in any electrolyte from which it displaces hydrogen when passing into solution. The above classification of metals according to the relative magnitude of their potentials in comparison with the discharge potential of hydrogen on them applies not only to the solution of metals, but also to their electrolytic deposition. Plating baths for depositing metals of the first class cannot be strongly acidified without causing the deposition of much hydrogen in place of an equivalent amount of metal; but a large proportion of acid may be added to solutions for the deposition of metals of the second class without greatly lowering the current efficiency through the deposition of hydrogen. J. F. S.

**Heat of Hydration of Gaseous Atomic Ions.** K. FAJANS (*Ber. Deut. physikal. Ges.*, 1919, **21**, 709—713. Compare this vol., ii, 12, 21).—A theoretical paper in which a correction of the heat of hydration of the hydrogen ion is made; in place of the previously published figure  $H^+ = 362$  Cal. per gram ion, the more correct, but still approximate, value 260 Cal. per gram ion is substituted. The term "hydration of ions" is more fully defined.

The term is not intended to indicate the formation of hydrates of the ions of definite stoichiometric composition, but rather that, due to the electrostatic charge of the ions, the oppositely charged part of the polar water molecule is turned toward the ion, and this in its turn exerts an attractive force on the next molecule. This type of dielectric polarisation proceeds continuously in the water surrounding the ion. The heat of hydration increases with decreasing volume of the gaseous ion, and reaches an exceedingly large value with the hydrogen ion.

J. F. S.

**Affinity of Halogen Atoms for Electrons and the Energy of Ionisation of the Hydrogen Haloids.** K. FAJANS (*Ber. Deut. physikal. Ges.*, 1919, **21**, 714—722. Compare preceding abstract).—A theoretical paper in which, making use of the principles previously published, the author calculates the energy change, in the form of a development of heat, which results from the combination of the halogen atoms with an electron. It is shown that the combination occurs with considerable loss of energy, but that the amount decreases with increasing atomic weight; the values found are in Cals.: chlorine 116, bromine 87, and iodine 81. The wave-length of the spectrum line brought about by this combination is calculated by means of the formula  $\epsilon = h\nu = h \times 3 \times 10^{10} / \lambda$ , in which  $\epsilon$  is the energy change and  $\lambda$  the wave-length in Ångström units. The following values are obtained: chlorine 2440, bromine 3350, and iodine 3490. By the same method of calculation, the work of ionisation of the hydrogen haloids has been obtained. The heat of combination of a gaseous hydrogen ion with a gaseous halogen ion is found to be: chlorine 322, bromine 310, and iodine 300 Cal. Using the formula  $V = 1000U / 96,500 \times 0.2388$ , in which  $V$  is the ionisation potential and  $U$  the energy change, the ionisation potential has been calculated, and the following values obtained: hydrogen chloride 14.0 volts, hydrogen bromide 13.4 volts, and hydrogen iodide 13.0 volts.

J. F. S.

**Electron Affinity of Gases.** K. FAJANS (*Ber. Deut. physikal. Ges.*, 1919, **21**, 723—727. Compare preceding abstracts).—In an earlier publication, Franck (A., 1910, ii, 817) attributes the loss of mobility of negative ions in the presence of oxygen and other gases to the combination of the gas atoms with electrons, and he formulates a potential series of the various gases. This question is discussed in the present paper. It is shown that the collision of an electron with a gas molecule effects the change represented by one of the equations: (1)  $X_2 + \ominus = X + X^-$ ; (2)  $X_2 + 2\ominus = 2X^-$ . For the halogens, the potential of the change is calculated, and the following values obtained: equation (1), chlorine -0.44 volt, bromine -1.78 volts, and iodine -1.96 volts; equation (2), chlorine -5.47 volts, bromine -5.55 volts, and iodine -5.47 volts. In the case of the hydrogen haloids, particularly hydrogen chloride, the change  $HX + \ominus = H + X^-$  is supposed to occur, and this, on calculation, yields the potentials: hydrogen chloride +0.39 volt, hydrogen bromide -0.09 volt, and hydrogen iodide -0.53 volt.

Both considerations explain the formation of gas ions from electrons and atoms without the necessity of assuming a specific electron affinity. J. F. S.

**Theory of Heat Change.** F. HABER (*Ber. Deut. physikal. Ges.*, 1919, **21**, 750—768).—A theoretical paper in which the author discusses the theory of heat change in connexion with (i) hydration energy of gaseous ions, (ii) energy of dissociation of salt vapours and ionisation potential of metal cations, and (iii) lattice energy and ultra-violet characteristic frequencies. J. F. S.

**Affinity of the Halogen Atoms towards Electrons.** M. BORN (*Ber. Deut. physikal. Ges.*, 1919, **21**, 679—685. Compare Born, A., 1919, ii, 214; Fajans, this vol., ii, 12).—A theoretical paper in which, based on the theory put forward previously by the author and Fajans (*loc. cit.*), the affinity of the halogen atoms for electrons is calculated. The values  $E$ , the energy of combination of an atom with an electron,  $Z$ , the energy of dissociation of an atom into ion and electron, and  $D$ , the heat of dissociation of a diatomic gas, are calculated, and the following numerical values in Cals. obtained: fluorine,  $Z = -26$  (mean); chlorine,  $Z = -62$  (mean),  $D = 57$ ,  $E = 119$  Cals., or 5.16 volts; bromine,  $Z = -61$ ,  $D = 23$ ,  $E = 84$  Cals., or 3.64 volts; iodine,  $Z = -59$ ,  $D = 18$ ,  $E = 77$  Cals., or 3.33 volts. It is shown, also, that the wave-length corresponding with the energy can be calculated on the basis of the quantum theory. The following wave-lengths in Ångström units are obtained: chlorine,  $\lambda = 2380$ ; bromine,  $\lambda_F = 3360$ ; iodine,  $\lambda_F = 3680$ . J. F. S.

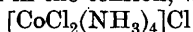
**Cuprous Oxide Photo-chemical Cell.** THEODORE W. CASE (*Trans. Amer. Electrochem. Soc.*, 1917, **31**, 351—364).—The action of light on one electrode of the cell  $\text{Cu}|\text{Cu}_2\text{O}|\text{aqueous copper formate} + \text{formic acid}|\text{Cu}_2\text{O}|\text{Cu}$  has been investigated. It is found that an *E.M.F.* up to 0.085 volt can be obtained and a current of 0.003 ampere if the metal plates are  $20 \times 3.2$  cm. in size. By arranging the cell on a rotating disk, so that the copper plates are alternately illuminated, an alternating current of various amplitudes and frequencies may be obtained. The action of the cell indicates that, under proper conditions, its life may be continuous, and that its elements will not disintegrate. The action of the cell is compared to the resistance change of the mineral cuprite when exposed to ultra-violet light. The contrast between the *E.M.F.* effect of cuprous oxide and cupric oxide is discussed. The action of the cuprous oxide photochemical cell is explained on the basis of the oxidation of cuprous oxide to cupric oxide in light. It is shown that there is no relation between the sign of the light action and the colour of heated copper plates. J. F. S.

**Determination of Hydrogen-ion Concentration.** JOHN W. M. BUNKER (*J. Biol. Chem.*, 1920, **41**, 11—14).—A modification of a bubbling electrode used in a closed vessel is fully described.

The apparatus is designed to meet the requirements of quick, accurate determinations in large numbers, and has given satisfactory results.  
J. C. D.

**Phenomenon after Anodic Polarisation. II.** A. SMITS, G. L. C. LA BASTIDE, and TH. DE CRAUW (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 296—299. Compare this vol., ii, '8).—It was previously shown that, on interrupting the current by which iron is polarised anodically, the potential of the iron falls, passes through a minimum, and then reaches the original value. This is due to diffusion changes, which affect the ratio  $\text{Fe}^{++}/\text{Fe}^{+++}$ . A similar phenomenon is now observed for nickel which has been anodically polarised. In solutions of nickel chloride, the minimum is reached in less than three seconds, whilst in the case of nickel sulphate, the change is much more prolonged. On cathodic polarisation of iron, the reverse phenomenon is observed, namely, the potential of the iron passes through a maximum and then falls to the normal value. This is to be expected if the explanation offered in the case of anodically polarised iron is correct. J. F. S.

**Polarisation Tension and Constitution of Complex Cobalt Compounds.** NILRATAN DHAR and G. URBAIN (*Compt. rend.*, 1920, **170**, 106—108).—The polarisation tension of a complex salt depends, not only on the constitution of the complex ion, but also on the nature of the ion which accompanies it. Thus, in the series starting with  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ , the replacement of ammonia by water causes a diminution in the tension, whereas in the series



the contrary holds good. The replacement of a molecule of water by a halogen in such a compound as  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$  causes a rise in the polarisation tension. Further, in the purpureo-salts, the tension is higher when the purpureo-complex contains a more negative radicle. The replacement of a chlorine atom by a nitro-group or of two chlorine atoms by a carbonato-group causes a lowering of the polarisation tension. The marked rise in the tension following on the substitution of an hydroxy-group for a chlorine atom is in agreement with the fact that these complex compounds are only stable in alkaline media.  
W. G.

**The Polarisation in Solutions of Iron.** W. ALBERT NOYES, jun. (*Compt. rend.*, 1920, **170**, 177—180. Compare this vol., ii, 9).—Nernst's formula,  $A = 0.0002T/m_1n_1$ , for calculating the value of  $A$  in the equation  $Ep = A \log_{10} I + B$ , giving the potential of an electrode traversed by a current, does not apply to the polarisation of solutions of ferrous salts, but none the less gives values proportional to the experimental values.  
W. G.

**Electrolytic Behaviour of Tungsten.** WALTER E. KOERNER (*Trans. Amer. Electrochem. Soc.*, 1917, **31**, 221—255).—The potential of tungsten in  $N$ -solutions of potassium cyanide, sodium hydroxide, potassium hydroxide, ammonium hydroxide, sulphuric

acid, hydrochloric acid, potassium nitrate, nitric acid, potassium fluoride, potassium chloride, potassium bromide, potassium sulphate, and potassium iodide has been measured against certain standard electrodes at 25°. The results show that tungsten does not behave as an insoluble electrode, but sends ions into the solutions with velocities which vary with the different solvents. Tungsten has a lower potential in *N*-alkalis than in *N*-acids, and a lower potential in *N*-acids than in *N*-salts. The following *E.P.* values ( $H=0$ ) are calculated from the experimental results; all solutions were normal: potassium cyanide,  $-0.647$  volt; sodium hydroxide,  $-0.316$  volt; potassium hydroxide,  $-0.315$  volt; ammonium hydroxide,  $-0.238$  volt; sulphuric acid,  $0.193$  volt; hydrochloric acid,  $0.256$  volt; potassium nitrate,  $0.300$  volt; nitric acid,  $0.311$  volt; potassium fluoride,  $0.522$  volt; potassium chloride,  $0.563$  volt; potassium bromide,  $0.589$  volt; potassium sulphate,  $0.719$  volt; and potassium iodide,  $0.733$  volt. A further series of *E.M.F.* measurements were made for tungsten in saturated solutions of tungstic acid in *N*-solutions of hydrochloric, sulphuric, and nitric acid respectively. The following values are obtained: hydrochloric acid,  $0.317$  volt; sulphuric acid,  $0.313$  volt; and nitric acid,  $0.317$  volt. The following combinations were also measured:

$W | W(OH)_6, N-H_2SO_4 || N-H_2SO_4 | W$ ,  $0.117$  volt;  $W | W(OH)_6, N-HCl || N-HCl | W$ ,  $0.057$  volt; and  $W | W(OH)_6, N-HNO_3 || N-HNO_3 | W$ ,  $0.009$  volt. The *E.M.F.* values obtained give the relative solubilities of tungstic acid in *N*-acid solutions. Analytically, the values were found to be: sulphuric acid,  $0.02281$  gram  $WO_3$  per litre; hydrochloric acid,  $0.01067$  gram  $WO_3$  per litre; and nitric acid,  $0.00025$  gram  $WO_3$  per litre. The anodic behaviour of tungsten has been investigated, and it is shown that in solutions of tungsten in acids it behaves as a cation, whilst in solutions of tungsten in alkalis it behaves as an anion. Tungstic acid goes into solution in acids and alkalis as an electrolyte, and not as a colloid. Tungsten dissolves anodically in aqueous and non-aqueous solutions of alkalis, acids, and salts. Under specified conditions, tungsten becomes passive when used as anode in aqueous and non-aqueous solutions of acids, bases, and salts. In aqueous solutions of alkalis and non-aqueous solutions of acids, bases, and salts, tungsten only becomes passive at high current densities (2 amperes per sq. dcm.). In aqueous solutions of acids and salts, the passive condition is assumed by tungsten at low current densities, and only at extremely low current densities will it remain active in these solutions. The passivity of tungsten is due to adherent films of hydrated oxides of tungsten. The films may be readily dissolved and the passivity destroyed. The hydrated oxide films appearing on the anode vary in colour from brown through blue to yellow. The degree of passivity varies with the colour of the films. The electrochemical equivalent of tungsten was found to be  $0.3173$  mg. per coulomb, a value very closely in agreement with the theoretical value. A number of experiments on the use of tungsten in storage cells are recorded. It is found



that the potential difference between the brown oxide (+) and the blue oxide (−) is 0.75 volt.

J. F. S.

**Electrical Endosmose and Adsorption.** T. R. BRIGGS, H. L. PIERSON, and H. S. BENNETT (*Trans. Amer. Electrochem. Soc.*, 1917, **31**, 257—270).—Using a modified form of Perrin endosmometer, which obviates the error produced by the evolution of gas at the electrodes and permits the use of diaphragms composed of powdered solids, the authors have determined the effect of the applied *E.M.F.* on the rate of flow of the liquid for the case of water with a glass diaphragm. In this case, the liquid flowed to the cathode, and the rate was found to be in keeping with Perrin's law for *E.M.F.* values lying between 530 and 100 volts. The effect of temperature on the rate of flow, using water and asbestos diaphragms and cellulose in boiled water, was determined at temperatures from 18° to 67°. It is shown that the product, rate  $\times$  viscosity<sup>-4</sup>, is practically constant. The flow of liquid in acid and alkaline solutions was investigated with alundum diaphragms, when sharp reversals were obtained, which are in keeping with Perrin's results. With glass diaphragms, no such reversal of direction was observed. The effect of barium ions on the rate of flow to the cathode in alkaline solutions is to reduce it much more than would an equivalent quantity of univalent ions. In acid solutions, barium ions have little effect, but sulphate ions reduce the rate much more than chloride, nitrate, or acetate ions. This with alundum and carborundum diaphragms. A number of experiments with dyes in *N*/500-solutions of hydrochloric acid and sodium hydroxide are described. It is shown that acid dyes (eosin, crystal ponceau) in alkali travel to the cathode, whilst basic dyes (safranine and methylene-blue) in acids travel to the cathode; acid dyes in acids and basic dyes in alkalis give indefinite results; alundum diaphragms were used in these experiments. The relationship between dyeing and electrical endosmosis tends to confirm the adsorption theory.

J. F. S.

**Chemistry of the Flaming Arc, in Relation to Luminescence.** WILLIAM ROY MOTT (*Trans. Amer. Electrochem. Soc.*, 1917, **31**, 365—390).—The light produced by flaming arcs containing various substances, and the relative volatility of refractory substances have been investigated. It is shown that there is no case of a blue arc shell. In every case except barium and vanadium, the arc core is blue or violet and the shell green, yellow, or red. Hence the light from the shell in every case but barium and vanadium is of longer wave-length than that of the arc core. The non-metallic elements, fluorine, chlorine, bromine, iodine, oxygen, sulphur, and nitrogen do not give elemental spectra, but fluorine, chlorine, oxygen, and nitrogen give the spectra of compounds in a carbon arc. The elements phosphorus, arsenic, and boron give only a few ultra-violet lines in the carbon arc. The easily reduced metals except those of the iron group yield no arc shell. The low energy of reac-

tion at high temperatures explains this lack of light. The most electropositive elements give the most markedly coloured luminous shells, especially where more than one valency stage is characteristic of the element at high temperatures. With yttrium oxide, the crater on the bead alone gives a green shell, which replaces the usual red shell obtained with the crater partly on the bead and partly on the carbon. Zirconium oxide gives a yellowish-white shell. The colour is probably due to hot solids, as zirconium carbide is less volatile than platinum, and its oxidation would give an extremely non-volatile oxide. Metallic zirconium is fairly volatile. In nearly every case with a carbon arc the flow of material is from positive to negative. With mixtures of salts of potassium, rubidium, and caesium fluoride respectively with calcium fluoride a strong blast also comes from the negative crater which causes a unique dimness near the negative part of the arc. A dim, large positive crater can often be produced by nearly all salts of potassium, rubidium, and caesium and by oxy-salts of sodium. This, with the effect on cyanogen bands and arc length may be explained by the reaction  $\text{KF} + \text{C}_2\text{N}_2 = \text{KCN} + \text{CNF}$ , and others necessary to return by oxidation to potassium fluoride, carbon dioxide, and nitrogen. A dim negative crater is most easily produced by barium salts volatilised from the positive crater. Glucinum oxide is the least volatile of the oxides which are so insulating as to prevent cratering, such as oxides of the alkaline earths, aluminium oxide and silica. The oxides of yttrium, zirconium, thorium, and the other rare earths allow cratering. Tungsten is by far the least volatile of the known elements, and this is followed by tantalum. The light of a yellow flame arc is due to reactions involving calcium fluoride, calcium oxide, calcium carbide, and metallic calcium.

J. F. S.

**Magnetism of the Metalammine Compounds.** ERNST ROSENBOHM (*Zeitsch. physikal. Chem.*, 1919, **93**, 693—720). —The magnetic susceptibility of a very large number of metallic ammine derivatives has been determined at 16—20° by means of a Curie torsion balance. The metals investigated were cobalt, platinum, rhodium, iridium, ruthenium, zinc, nickel, copper, and chromium. The ammine derivatives of cobalt, platinum, iridium, rhodium, zinc, and ruthenium are, except in the case of some of the cobalttriammines, diamagnetic. The diamagnetism is greatest in hexammine salts of cobalt, somewhat less in the pentammine derivatives, very much less in the tetra-ammine derivatives, and least in the triammine derivatives of cobalt. In the last class of compounds it is found occasionally that paramagnetism is exhibited. The same regularity is observed when the whole or a portion of the ammonia group is replaced by ethylenediamine or propylenediamine. The entrance of one or more ionogen residues into the sphere of the metallic atom is shown to be followed by a decrease in the diamagnetism in the case of all the diamagnetic metallic ammines investigated. In the case of platinum it is shown that the susceptibility and molecular magnetism of

bivalent platinum is less diamagnetic than is the case with quadrivalent platinum. Further, as in the case of the electro-conductivity, in passing from hexammino- to hexacido-derivatives, the magnetism passes through its extreme value with those compounds which have no ionogen acid residue. The ammine derivatives of nickel, copper, and chromium are paramagnetic. In the case of the chromium derivatives it is shown that the magnetic susceptibility and the molecular magnetism are least in the hexammine derivatives and increase steadily to the triammine derivatives. As in the case of the cobalt derivatives the extreme value occurs with those derivatives which contain no ionogen acid group. The examination of the geometrical isomerides of the derivatives of cobalt, platinum, and chromium indicates that magnetically the *cis*- and *trans*-forms of a given compound cannot be differentiated. At the same time it is shown that the measurement of the magnetic susceptibility is a very sensitive method of testing the purity of these isomerides. In the case of the optical isomerides of cobalt and chromium, it is shown that the *d*- and *l*-forms have the same susceptibility, whilst the racemate has a different value. In most cases the susceptibility of the racemate is smaller than that of the active isomerides, but this is not always so. In the case of the co-ordination isomerides of cobalt and chromium, it is found that the susceptibility is not alike, but in most cases the two values are not very different. The greatest difference is found in the case

$$[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{C}_2\text{O}_4)_3]\chi \cdot 10^6 = 18.80;$$

$[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{C}_2\text{O}_4)_3]\chi \cdot 10^6 = 13.75$ . The difference observed between the co-ordination isomerides and the other types of isomerides is probably due to the fact that the two nucleus atoms are magnetically opposed to one another, the one acting diamagnetically and the other paramagnetically. An examination of the magnetic influence of the nucleus atom shows that metalammines, with a metal valency which is stable in the normal salts, possess a susceptibility of the same order as the normal salts, whilst metalammines, with a metal valency which is unstable in the normal salts, may have a susceptibility very different from that of the normal salts, and it may even be of the opposite sign. Measurements of the polynuclear cobalt and chromium ammines show that these compounds are quite normal in their magnetic relationships. The molecular magnetism is calculated from Pascal's formula,  $M = \Sigma A + 1$  (*A.*, 1911, ii, 91), and the values compared with the present measurements. It is found that both sets of values are remarkably close. The magnetic properties are considered in connexion with the magnetone, and it is shown that in accordance with Weiss's theory the magnetone number is always a whole number. J. F. S.

**A Thermoregulator with the Characteristics of the Beckmann Thermometer.** R. B. HARVEY (*J. Biol. Chem.*, 1920, 41, 9—10).—The instrument can be set easily at any temperature desired between  $-20^\circ$  and  $+250^\circ$ . The electrical contacts are placed so that small temperature changes will make or break the circuit. When run on test in an air-bath with a standard Beckmann

thermometer and vigorous stirring, the air temperature was regulated to within  $\pm 0.004^\circ$ .  
J. C. D.

**Specific Heat of Sulphuric Acids, Nitric Acids, and their Mixtures.** PAUL PASCAL and M. GARNIER (*Bull. Soc. chim.*, 1920, [iv], 27, 8—18).—Using an electrical method of heating, the authors have determined the specific heats of binary mixtures of sulphuric acid and water containing from 10 to 100% of sulphuric acid, of binary mixtures of nitric acid containing from 10 to 98% of nitric acid, of binary mixtures of nitric and sulphuric acids, and of ternary mixtures of nitric and sulphuric acids and water. The results are set out in detail, and a graph with trilinear co-ordinates combines the data.  
W. G.

**Latent Heat and Surface Energy.** G. RUDORF (*Phil. Mag.*, 1920, [vi], 39, 238—239).—A criticism of Hammick's paper under the above title (A., 1919, ii, 389), in which it is shown that using more accurate values for  $\gamma$  (surface tension),  $\sigma$  (molecular diameter), and  $L_i$  (internal latent heat), the values of  $\gamma V/J\sigma$  and  $L_i/6$  give results which are widely divergent in the case of argon. The values calculated by the author are 302 and 240 respectively, instead of 226 and 214 calculated by Hammick.  
J. F. S.

**Critical Constants. Critical Temperature of Hydrogen Bromide.** E. MOLES (*J. Chim. Phys.*, 1919, 17, 415—424).—A criticism of Fielding's work (compare A., 1919, ii, 45) in which the author supports the law of Guldberg and Guye as to the relationship between the absolute critical temperature and the absolute boiling point/760 mm.

For hydrogen bromide the author finds experimentally the value  $89.80^\circ$  for the critical temperature, and the value as calculated by Guldberg and Guye's rule is in reasonably close agreement with this.

He further indicates that Fielding's formula (*loc. cit.*) for calculating the critical pressure gives results considerably higher than those found by experiment in the cases of hydrogen chloride and hydrogen sulphide.  
W. G.

**Form and Regularities of the Vapour Pressure Curve.** E. WERTHEIMER (*Ber. Deut. physikal. Ges.*, 1919, 21, 692—708).—A theoretical paper in which it is shown that the previously published vapour-pressure formula,  $p + Ap^2 = CT^n$  (*ibid.*, 1919, 21, 435), contains in itself five approximation laws dealing with the saturation state, namely, Dühring's rule of constant boiling-point difference, the law of analogous state, Trouton's rule of normal heat of vaporisation, the constancy of the van der Waals' number ( $f$ ) at the critical point, and the Nernst equation for calculating chemical constants. These expressions are all developed from the above formula, and examined by means of a large number of previously published examples.  
J. F. S.

**Vapour Pressure Regularities.** W. HERZ (*Zeitsch. Elektrochem.*, 1919, **25**, 408—409. Compare A., 1919, ii, 218).—According to the theory of corresponding states, the proportionality factor  $a$  in van der Waals's equation,  $\log \pi_0/p = a(\delta_0/T - 1)$ , where  $\pi_0$  is the critical pressure,  $\delta_0$  the critical temperature (in absolute units), and  $p$  and  $T$  corresponding values of pressure and temperature, should for all normal substances have the constant value 3. The value of  $a$  has been calculated for the elements hydrogen, nitrogen, oxygen, mercury, argon, krypton, xenon, chlorine, and bromine, and in most cases it is nearer 2 than 3, and is always less than 3. In vertical series the value increases with the atomic weight of the element. The value of the constant has also been calculated for the hydrocarbons pentane to decane, acetic and propionic acids, a number of alkyl esters of fatty acids, and some alkyl chlorides, in some cases for a number of different temperatures. In all these cases its value is close to 3. It may rise or fall with increasing temperature, and in most cases shows a distinct rise as a homologous series is ascended. Associated liquids show a greater value for  $a$  than similarly constituted non-associated liquids. Thus the value for water is greater than that for hydrogen sulphide, and that for ammonia greater than that for phosphine. E. H. R.

**Relative Volatilities of Refractory Materials.** WM. ROY MOTT (*Trans. Amer. Electrochem. Soc.*, 1918, **34**, 255—295).—Ten arc methods of ascertaining the relative volatilities of metals, carbides, oxides, nitrides, fluorides, chlorides, and sulphides are suggested and to some extent developed. The most rigid method depends on the least volatile material remaining as the residue when distilling mixtures. For materials boiling above the boiling point of iron saturated with carbon (3500°) a series of boiling points has been estimated on a triple basis of reference, namely, reference to the curves for iron for equal atomic amounts of material, fractional distillation series, and position of deposition at the negative arc crater. The boiling points in the series are: iron saturated with carbon, 3500°; silica, 3500°; palladium, 3600°; carbon, 3700°; alumina, 3700°; chromium carbide, 3800°; vanadium carbide, 3900°; rhodium, 4000°; platinum, 4050°; uranium carbide, 4100°; ruthenium, 4150°; lanthanum oxide, 4200°; titanium carbide, 4300°; yttrium oxide, 4300°; columbium carbide, 4300°; zirconium oxide, 4300°; thorium oxide, 4400°; iridium, 4400°; osmium, 4450°; molybdenum carbide, 4500°; yttrium carbide, 4600°; thorium carbide, 5000°; zirconium carbide, 5100°; tantalum carbide, 5500°; tungsten carbide, 6000°. Tungsten allows carbon to distil rapidly through its molten carbide, which probably surrenders carbon vapour exactly as copper oxides surrender oxygen. The boiling point of tungsten is estimated at 6000° and that of tantalum at 5500°. Zirconium carbide is the least volatile carbide, and is followed by thorium carbide. Thorium oxide is the least volatile oxide, whilst the white and yellow oxides of zirconium are nearly as non-volatile. The least volatile non-cratering oxide is glucinum oxide (b. p. 3900°), which is left as a final residue in fractional

distillation of its mixtures with barium oxide, strontium oxide, calcium oxide, magnesium oxide, silica, and alumina. From the crater distances at positive and negative, the boiling points of the more common refractory oxides are estimated as follows: barium oxide, 2000°; titanium oxide, below 3000°; chromium sesquioxide, 3000°; calcium oxide, 3400°; silica, 3500°; magnesia, 3600°; alumina, 3800°; and glucinum oxide, 3900°. "Smoke time" estimates of boiling points are given for several oxides, sulphides and halogen salts. The figures are only roughly approximate. The volatility of oxides follows the increasing order: potassium, sodium, lithium, vanadium, boron, barium, strontium, manganese, iron, cobalt, nickel, chromium, titanium, silicon, calcium, magnesium, aluminium, erbium, cerium, neodymium, lanthanum, zirconium, and thorium. The characteristic oxide is intended in every case. Boron nitride sublimes at about 3000°. As an addendum to the paper is added a bibliography of work on the volatilisation of refractory materials, and where in these papers figures are given for boiling points and melting points these are recorded. A further addendum deals with the ratio of the melting point to the boiling point. These values are given for practically the whole of the elements, and it is shown that with the exception of the metals of the first group of the periodic system the ratio abs. b. p./abs. m. p. = ca. 1.8.

J. F. S.

**Glass Rectifying Column especially suitable for the Rectification of Liquid Mixtures and the Recovery of Volatile Solvents.** W. ELSNER (*Chem. Zeit.*, 1920, **44**, 11—12).—

The apparatus consists of a glass column 50 mm. in diameter and filled with glass balls, the surfaces of which are ground or etched. A perforated plate at the bottom of the column serves as a support for the balls, and the latter are of three sizes, the lower part of the column containing the largest balls, whilst the smallest balls form the uppermost layers. The top of the column is connected with a small glass dephlegmator provided with a water jacket, which is supplied from a constant-level reservoir, and above the dephlegmator is a still-head carrying a thermometer and a side-tube, which is connected with a condenser. All parts of the apparatus are connected together by means of ground-in joints.

W. P. S.

**Saturation Pressure, calculated from the Temperature, Latent Heat of Vaporisation, and the Molecular Volume of the Liquid by means of Maxwell's Distribution of Velocities Law.**

K. K. JÄRVINEN (*Zeitsch. physikal. Chem.*, 1919, **93**, 743—753).—A theoretical paper wherein equations are deduced by means of which the saturation pressure may be calculated. These equations have the form

$$c_2 = c_3 / c = \sqrt{(2W_i + 3RT)/M} : \sqrt{3RT/M} = \sqrt{(2W_i/3RT) + 1},$$

and  $z = p/p_a$ , in which  $z$  is the number of molecules which have a velocity  $c$ ,  $c_2$  is the mean velocity of the molecules,  $p$  is the

saturation pressure,  $p_a$  the internal pressure, and  $W_i$  the internal latent heat of vaporisation. The remaining symbols have their usual significance. The expression has been tested on the substances oxygen, nitrogen, benzene, ether, *n*-pentane, toluene, and methyl butyrate, and a fair agreement with fact obtained.

J. F. S.

**Molecular Attraction. IV.** K. K. JÄRVINEN (*Zeitsch. physikal. Chem.*, 1919, **93**, 737—742. Compare preceding abstract, and A., 1913, ii, 293; 1915, ii, 251; this vol., ii, 90).—A theoretical paper in which the author recalculates the constants used in the formulæ previously published (*loc. cit.*). It is found for monatomic molecules that  $n=5$  and  $a=55.06$ .  $W_i \cdot v^{\frac{1}{3}} = 41.30 \cdot C_a v^{\frac{1}{3}}/a$ . In the case of polyatomic molecules, the molecular attraction is represented by the expressions  $F = m^2 k / (r - \beta r_0)^n = m^2 k / (v^{\frac{1}{3}} - \beta v_0^{\frac{1}{3}})^n$ . From this equation, the following expressions are deduced:

$a = (n-1)/3 \cdot W_i (v^{\frac{1}{3}} - \beta v_0^{\frac{1}{3}})^{n-1} = C_a (v^{\frac{1}{3}} - \beta v_0^{\frac{1}{3}})^n / v^{\frac{1}{3}} \cdot a$  and  $C_a/a \cdot W_i = (n-1)/3 \cdot v^{\frac{1}{3}} / (v^{\frac{1}{3}} - \beta v_0^{\frac{1}{3}})$ . In these expressions, the symbols have the meaning previously applied to them,  $r_0$  is the smallest distance between the molecules, and  $v_0$  the smallest volume;  $n=5$  and  $\beta=0.242$ , whence  $C_a/a \cdot W_i = 4/3 \times 1.27 = 1.69$ . A number of substances on which the formulæ have been tested give the constant 1.69, and agree most nearly with the value  $n=5$ . J. F. S.

**Method of Calculating the Limits in Physico-chemical Phenomena.** MAURICE PRUD'HOMME (*J. Chim. phys.*, 1919, **17**, 377—382).—The method previously employed for calculating the critical temperature in terms of the surface tension (compare A., 1919, ii, 183) is shown to be applicable for calculating the density at absolute zero as a function of the temperature in the case of gases, and it is shown that, as in the case of liquids, the density at absolute zero is four times the critical density. The critical pressure may also be calculated as a function of the temperature, subject to a correction of  $8^\circ$ , the calculated value being too high. W. G.

**Molecular Condition of Liquids and Solutions.** ERNST KRÖBER (*Zeitsch. physikal. Chem.*, 1919, **93**, 641—692).—Density determinations have been made at  $25^\circ$  of a large number of solutions of liquids in organic solvents, and of a number of solid substances in solid solvents. The number of molecules of solvent replaced by one molecule of the dissolved substance in unit volume is calculated in each case. It is shown that the number of replaced molecules is approximately equal only when the dissolved substance belongs to a closely related group, for example, the mono-substitution derivatives of benzene. In all other cases, different numbers of molecules of the solvent are replaced; the respective figures are approximately in the same proportion as the molecular volumes, and the relationship is only slightly dependent on the nature of the solvent and the concentration of the dissolved substance. The behaviour of solutions of solids at various temperatures has been

investigated. The volume changes accompanying the solution of liquids is small, and is not specific either in the case of solvent or dissolved substance. In the case of solids dissolved in liquids, the positive volume changes are larger, and in general appear to be due to a change in the state of aggregation. In most cases, a characteristic behaviour is observed, both with the solvent and the dissolved substance. The coefficient of compressibility and the coefficient of expansion run parallel with the mean atomic concentration and the reciprocal of the mean atomic volume. In homologous series, the atomic concentration, corresponding with constant atomic volume, is nearly constant at the boiling point, and for all substances which contain only carbon, hydrogen, and oxygen the value fluctuates only between very narrow limits. It appears possible, from the properties of a mixture, particularly from the coefficient of expansion, to decide whether a contraction or an expansion will take place. In the very large number of cases examined, only three cases were exceptional to the rules formulated, and in all probability these cases were abnormal, because of a chemical reaction between the components. J. F. S.

**Viscosity Measurements.** O. FAUST (*Zeitsch. physikal. Chem.*, 1919, **93**, 758—761).—The influence of the diameter of the tube on the viscosity of liquids has been investigated in connexion with the method of viscosity measurements made by determining the time required for a bubble of air to rise through a measured length of the liquid. It is shown that  $Q = \pi(r^2 - r_1^2)$ , in which  $r$  is the radius of the tube,  $r_1$  the radius of the air bubble, and  $Q$  the cross-section of the liquid between the bubble and the tube. Since  $(r - r_1)$  is constant and  $r + r_1 = 2r$ ,  $Q = 2\pi r \times C$ , where  $C$  is a constant. The formula is tested with a viscid oil with tubes of various diameters, and the measured time compared with the calculated time. It is shown that with wider tubes (18—24 mm.) the calculated and observed results agree, but with narrower tubes (16—12 mm.) there is an increasing divergence with decreasing diameter. This is due to the fact that the error introduced by placing  $r + r_1 = 2r$  is greater in the case of narrow tubes than in the case of wider tubes. It is also shown that in the case of wider tubes, the time required for the ascent of the bubble is independent of the size of the bubble, whilst the same is almost true with narrower tubes. J. F. S.

**The Welding of Solid Powders under Pressure.** TONI VON HAGEN (*Zeitsch. Elektrochem.*, 1919, **25**, 375—386).—An extensive series of experiments is described on the cohesive properties of pure powdered inorganic substances under pressure. The substances examined include the oxides, sulphides, sulphates, halogenides, nitrates, and carbonates of many metals, including both anhydrous and hydrated forms of the salts. Fine-grained particles were found to cohere better than coarser, and for most experiments the substance was ground to pass a sieve of 25 meshes per sq. mm. The



powder was subjected, for most experiments, to a pressure of 560 kilos. per sq. cm. in a screw press, and the tablets formed were examined by inspection, and, where possible, by determining their hardness or crushing strength. The substances showing the best cohesion gave tablets which appeared homogeneous. Among these were the halogenides of the alkali metals and silver and hydrated calcium chloride. The next class gave tablets with smooth surfaces and pulverulent bodies, this class including the hydrated sulphates of aluminium, zinc, cobalt, and sodium, many nitrates and sulphides, and the oxides of lead. Most of the oxides gave powdery bodies of low crushing strength, whilst the anhydrous sulphates of potassium, calcium, strontium, barium, and lead, and the carbonates of cadmium, barium, and lead showed no cohesion at all. Generally, substances of very high melting point and very hard substances show little cohesion. A cohesive substance mixed with a non-cohesive substance improves the binding properties of the latter, but quantitative experiments on the hardness of mixed tablets showed that this was not proportional to the composition. In the case of cohesive substances, increasing pressure increases the density of the tablet, rapidly at first, then slowly as the maximum is approached. The maximum may rise to the true density of the crystalline substance, as in the case of gypsum, or it may approach very nearly to this value, as with sodium and potassium chlorides.

The experiments show that there is a close relation between the crystalline form of a substance and its behaviour under pressure. Those substances which give the most homogeneous bodies under pressure are those which have plastic crystals, that is, the crystals of which contain glide-planes and are deformable without losing their structure. The above substances, which give, under high pressure, tablets having almost the maximum possible density, have been shown to have plastic crystals. On the other hand, the crystals of such substances as quartz and barium sulphate show no trace of plasticity, and their powders show no cohesive properties. [See also *J. Soc. Chem. Ind.*, 1920, 189A.] E. H. R.

**Absorption of Gases by Charcoal. I. Variations due to Heat Treatment, Pre-equilibrium Effects.** HARVEY B. LEMON (*Physical Rev.*, 1919, 14, 281—292).—The rate at which coconut-shell charcoal absorbs air, and the total amount it can absorb, may be widely varied by varying the heat treatment. This paper considers the case in which the mass of air used is less than that required for saturation. Increase in activation is produced by repeated exhaustions at 650°, each exhaustion being followed by an absorption of air at the temperature of liquid air. Decrease in activation results if a temperature of 800—900° is used. Two hypotheses to account for this, (1) the clogging of the pores by heavy hydrocarbons, removed by flushing out with gas, and (2) the alteration in the fineness of the carbon from the point of view of a saturated solution of carbon in liquid gas, are discussed, but found inconclusive, particularly inasmuch as removal of the heavy hydro-

carbons by light petroleum, alcohol, and acetone causes loss in efficiency.

CHEMICAL ABSTRACTS.

**Absorption of the so-called Surface Active Substances by Various Absorbents.** LEONOR MICHAELIS and PETER RONA (*Kolloid Zeitsch.*, 1919, **25**, 225—229).—Comparative absorption experiments have been carried out with charcoal, kaolin, osmosil (a commercial silicic acid preparation), talc, amorphous silicon, ferric hydroxide, freshly precipitated manganese dioxide, calomel, barium sulphate, and calcium carbonate as absorbents for acetone, tributyrin, heptyl alcohol, and octyl alcohol. It is shown that no carbon-free absorbent has a power of absorption that even approaches the absorptive power of charcoal for surface active non-electrolyte substances. In most cases there is no absorption, in others only the merest trace of absorption takes place. Talc comes next to charcoal in its absorption of these substances. J. F. S.

**Osmosis and Diffusion of Ions through a Polarised Septum. Physical Methods for the Study of Cellular Nutrition.** PIERRE GIRARD (*J. Chim. Phys.*, 1919, **17**, 383—408).—A résumé of work already published (compare A., 1908, ii, 456; 1909, ii, 463, 537; 1911, ii, 860; 1914, ii, 718; 1919, i, 419, 461) and a reply to Hamburger (compare A., 1917, ii, 562). W. G.

**Theory of Solution and Suspension.** RICHARD ZSIGMONDY (*Kolloid Zeitsch.*, 1920, **26**, 1—10).—A theoretical paper in which the significance of the terms "solution" and "suspension" is discussed at length. J. F. S.

**Physical Chemical Analysis of Metallic Oxide Sols.** WOLFGANG PAULI (*Kolloid Zeitsch.*, 1920, **26**, 20—23).—Polemical. An answer to Zsigmondy's theory of solutions and suspensions (preceding abstract), which is based on the work of Pauli and Matula (A., 1917, ii, 563). J. F. S.

**Nomenclature of Colloids.** G. WEISSENBERGER (*Kolloid Zeitsch.*, 1919, **25**, 230).—The author points out that the term "gel" is applied both to jellies and to the products of coagulation. He suggests that the term gel should be retained and used only in connexion with jellies, and that the products of coagulation should be termed *coagels*, thereby implying that they belong to the group of coarse, disperse colloids. J. F. S.

**Rôle of Valency in Coagulation by Electrolytes, particularly in the Case of the Suspensoids.** WOLFGANG OSTWALD (*Kolloid Zeitsch.*, 1920, **26**, 28—39).—A theoretical paper in which the various views put forward in connexion with the part played by the valency of the electrolyte ions in the coagulation of colloids is critically discussed. J. F. S.

**Coagulation of Clay and the Protective Effect of Humic Acid.** SVEN ODÉN (*J. Landw.*, 1919, **67**, 177—208).—An extensive review is given of previous work on clay suspensions as regards their aggregation, sedimentation, disintegration, swelling value, and nature of individual particles. Experiments were made by the author with suspensions of two clays of different character, purified by dialysis, and diluted with conductivity water to about 1% strength. Varying amounts of colloidal humic acid were added to 10 c.c. of each suspension, and the effect on coagulation noted. It was found that the minimum amount required to produce a protective effect on the addition of ammonium nitrate solution as coagulant was 0.065 mg. in one case and 0.14 mg. in the other. On varying the coagulant, it was found that much larger amounts of humic acid were required to prevent coagulation with barium nitrate and caesium chloride than with ammonium nitrate and lithium chloride. The author concludes that the protective effect of humic acid is of the same order as that of other colloids, but that it is greatly affected by the electrolyte concentration, owing to the extreme sensitiveness of colloidal humic acid to electrolytes. The effect appears to be specific for different clays and electrolytes, so that a proper explanation of the effect is still uncertain. It is clear, however, that it depends on an absorption of the protective substance by the particles to be protected. J. H. J.

**Non-, Uni-, and Bi-variant Equilibria. XIX.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 318—322. Compare A., 1917, ii, 454).—A further theoretical paper dealing with the conditions of equilibrium in non-variant, uni-variant, and bi-variant systems. The present paper deals with the equilibria of  $n$  components in  $n+1$  phases. J. F. S.

**Characteristic Case of Rhythmic Crystal Arrangement.** M. HOFSSÄSS (*Zeitsch. physikal. Chem.*, 1919, **93**, 754—757).—A few drops of the  $N/10$ -sodium hydroxide which had been used to absorb the carbon dioxide produced in the combustion of artificial graphite was allowed to evaporate on a microscope slide. The crystals formed, when magnified 500 times, showed a striking rhythmic, concentric arrangement. Each series of rings commences from a crystal nucleus, around which circles of crystals 0.002 mm. apart are formed. In all other cases of combustion of coal, lignite, and wood, the crystals produced from the sodium hydroxide wash-bottle exhibited the usual dendritic forms. J. F. S.

**The Rate of Decomposition of Malonic Acid.** CYRIL NORMAN HINSHELWOOD (*T.*, 1920, **117**, 156—165).

**Mechanism of the Addition of Hydrogen to Unsaturated Glycerides in the Presence of Finely Divided Nickel.** R. THOMAS (*J. Soc. Chem. Ind.*, 1920, **39**, 10—18T).—The rate of hydrogenation of olive oil (iodine value, 86) by means of hydrogen

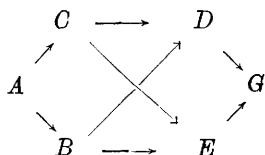
in the presence of finely divided nickel has been determined at 120°, 150°, and 180°. As the olive oil contained 7% of linolin, equations are deduced for the rate of addition of hydrogen by mixtures of unsaturated glycerides. The reaction between pure hydrogen at constant pressure and a single unsaturated glyceride takes place according to the equation for reactions of the first order. The more highly unsaturated glyceride linolin absorbs hydrogen very much faster than olein. The rôle played by the catalyst is discussed from the results of experiments on the influence of pressure of hydrogen and of temperature on the velocity of reaction. It is found that the rate of saturation of olein (with three double bonds) is proportional to  $p^{\frac{1}{2}}$ , where  $p$  is the pressure of hydrogen. This is in keeping with the view that hydrogen becomes active through its absorption by the catalyst, with a dissociation of the hydrogen molecules into atoms. The temperature-coefficient of the velocity constant is small; an increase of 10° in temperature over the range 120—180° increases the velocity 1.13 times. This suggests a photochemical reaction, the molecules of olein being brought into an active condition by absorption of infra-red radiation emitted by the catalyst. The mode of action of gaseous catalyst poisons is illustrated and discussed. Such action may be a purely physical one, or it may be chemical in the sense that the poison is capable of reacting either with or in the presence of the catalyst.

J. F. S.

**Hydrolysis of Esters of Polyhydric Alcohols.** EIICHI YAMAZAKI (*J. Tokyo Chem. Soc.*, 1919, **40**, 498—514).—Denoting the five mono-, di-, and tri-acetins by

- (A)  $\text{OAc}\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CH}_2\cdot\text{OAc}$ ,  
 (B)  $\text{OAc}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OAc}$ , (C)  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CH}_2\cdot\text{OAc}$ ,  
 (D)  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OAc}$ , and  
 (E)  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CH}_2\cdot\text{OH}$ ,

glycerol (G) is obtained from triacetin by hydrolysis along the following routes (annexed formula).



This apparently complicated system of hydrolysis of triacetin can be studied in a simple manner, since all esters containing  $\text{R}\cdot\text{CO}\cdot\text{O}\cdot$  have approximately the same constant of velocity of hydrolysis, which is independent of the position of the acid group in the polyhydric alcohol. The constants of velocity of hydrolysis of tri- to di-acetin ( $K_1=0.00638$ ) and of di- to mono-acetin ( $K_2=0.00423$ ) by hydrochloric acid, calculated from Geitel's data (A., 1897, ii, 547; 1898, ii, 330), are compared with the velocity constant ( $K_3=0.002213$ ) for monoacetin  $\rightarrow$  glycerol. Assuming that each acetoxy-group is hydrolysed at the same rate,  $K_1/3=K_2/2=K_3(=K)$ . The following equations are thus derived:  $c_{M_1}=c_0e^{-3Kt}$ ;  $c_{M_2}=3c_0(1-e^{-Kt})e^{-2Kt}$ ;  $c_{M_3}=3c_0(1-e^{-Kt})^2e^{-Kt}$ ; and  $c_{M_4}=c_0(1-e^{-Kt})^3$ , where the concentrations of the three acetins and of

glycerol are denoted by  $c$  with suffixes  $M_1$ ,  $M_2$ ,  $M_3$  and  $M_4$  respectively. If free acetic acid is denoted by  $c_A$ , then

$$c_A = c_{M_2} + 2c_{M_3} + 3c_{M_4} = 3c_0(1 - e^{-kt})^3.$$

A satisfactory agreement is recorded between the calculated and the observed values of  $c_A$  at any instant. CHEMICAL ABSTRACTS.

**The Factors of Diazotisation.** E. TASSILLY (*Bull. Soc. chim.*, 1920, [iv], 27, 19—33).—Using the method previously described (compare A., 1914, ii, 256), the author has studied the rate of diazotisation of a number of amines. The reaction has been previously shown to be bimolecular. Doubling the acidity of the solution does not modify the process of diazotisation in the case of aniline. The diazotisation of sulphanilic acid is much more rapid when the concentration of the reacting solutions is increased, and it is favoured by an excess of sodium nitrite. The stability of a diazo-compound with respect to time and temperature may be studied by this method. W. G.

**Colour Change of Congo-rubin under the Influence of Reactions and Neutral Salt Action.** HEINRICH LÜERS (*Kolloid Zeitsch.*, 1920, 26, 15—20).—The time required by solutions of congo-rubin (0.01%) to change from red to the intermediate colour between red and blue in the presence of hydrogen ions of various concentrations and in the presence of neutral salts has been determined. It is shown that with  $H^+ = 5.5 \times 10^{-5}$  the change is instantaneous, but with decreasing hydrogen-ion concentration the time increases rapidly until, with the value  $H^+ = 6.8 \times 10^{-6}$ , it is practically infinite. In the presence of a neutral salt (KCl) very small hydrogen-ion concentrations cause the change to take place very rapidly. The presence of large quantities of neutral salts increases the activity of the indicator toward hydrogen ions about seventy times. In the presence of hydroxyl ions, neutral salts decrease the activity of the indicator until, with  $OH' = 10^{-2}$ , it no longer undergoes the colour change. These changes are explained by a change in the condition of solvation of the indicator brought about by the electrolyte. J. F. S.

**Catalysis.** MATHEUS D'ANDRADE ALBUQUERQUE (*Revista chim. pura applic.*, 1918, 3, reprint 22 pp.).—After reviewing the theories which have been formulated on the subject of catalysis, the author advances the view that catalysis is due to the formation of intermediate compounds ("catalides") as a result of residual affinity. This does not apply to cases where the intermediate compound is a salt, or to catalysis by solvents, finely divided (colloidal) metals, or organic ferments. W. R. S.

**Whole Number Isotopes and Allied Phenomena.** F. H. LORING (*Chem. News*, 1920, 120, 73—77).—A theoretical paper in which the experimental evidence supporting the idea of whole number isotopes is given, together with the spectroscopic examin-

ation of isotopes. The photoelectric effect in its connexion with isotopes is discussed, as well as the cyclic evolution of elements and isotopes. A table is given in the paper indicating the percentage of higher mass isotopes of the commoner elements. The whole discussion tends to show that the whole number isotopes are a reality, and that the isotopic proportions may modify the electrical properties of the elements.

J. F. S.

**Deduction of the Chemical Constants of Polyatomic Gases from Planck's Theory of Probability.** LÉON SCHAMES (*Physikal. Zeitsch.*, 1920, **21**, 38—39).—A mathematical paper in which a method of deducing the chemical constants of tri- and tetra-atomic gases is deduced. The results are compared with those deduced by Sackur (A., 1913, ii, 128) and Tetrode (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1167).

J. F. S.

**Chemical Constants ; Moment of Inertia of the Molecule and the Quantum Theory of Gases.** LÉON SCHAMES (*Physikal. Zeitsch.*, 1920, **21**, 39—42. Compare preceding abstract).—The chemical constant  $i_e$  and the moment of inertia  $P \cdot 10^{40} = \sqrt[3]{PQR}$  have been calculated by means of the equations previously developed (*loc. cit.*) for oxygen, carbon monoxide, nitrogen, carbon dioxide, and water. The following values for the moment of inertia are obtained: oxygen, 31.2; carbon monoxide, 10.07; nitrogen, 9.91; carbon dioxide, 5.80; and water, 1.365. The results are compared with the values of other investigators, particularly those of Langen (A., 1919, ii, 183), and found to be in very good agreement.

J. F. S.

**A Cheap and Simple Microbalance.** J. H. SHAXBY (*Proc. Physical Soc. London*, 1919, **32**, 21).—A balance for loads from 5 mg. to 5 dcg., depending on the depression of a stretched thread, is described.

J. R. P.

**Condensers.** FRITZ FRIEDRICHS (*Zeitsch. angew. Chem.*, 1920, **33**, 29—32).—A critical discussion of the various forms of laboratory condensers which have been described in literature from the time of Liebig onwards. As regards efficiency, the screw-shaped condensing tube, with five "threads" and provided with an internal cooling jacket, gives the best results. This form of condenser is more suitable for use as a reflux apparatus than is the spiral form.

W. P. S.

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## Inorganic Chemistry.

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**Oxidation of Sulphurous Acid by Ferric Salts.** JULIUS MEYER (*Ber.*, 1920, **53**, [B], 77—78).—In Houben's recent method for the estimation of ferrous and ferric iron together in acid solutions, the assumption is made that when a ferric salt is reduced by sulphur dioxide the increased acidity corresponds with two-thirds of the acid in combination with the ferric iron, according to the equation  $2\text{FeCl}_3 + \text{SO}_2 + 2\text{H}_2\text{O} = \text{FeSO}_4 + \text{FeCl}_2 + 4\text{HCl}$  (this vol., ii, 56). It is now stated that the reduction of a ferric salt most probably proceeds in stages; thus, first, a red ferric ferrisulphite,  $\text{Fe}[\text{Fe}(\text{SO}_3)_3]$ , is formed, which slowly changes in the cold, more quickly on warming, into the ferrous salt, not, however, with the production of sulphuric acid, but dithionic acid, thus:  $\text{Fe}[\text{Fe}(\text{SO}_3)_3] = \text{FeS}_2\text{O}_6 + \text{FeSO}_3$ . Before any increase in the acidity can take place, therefore, the dithionate must be decomposed, thus:  $\text{FeS}_2\text{O}_6 + \text{H}_2\text{O} = \text{FeSO}_4 + \text{H}_2\text{SO}_3$ , and it is not quite certain whether this is completed even by vigorous boiling. J. C. W.

**The Advantages of the Synthesis of Ammonia at Very High Pressures.** GEORGES CLAUDE (*Compt. rend.*, 1920, **170**, 174—177. Compare this vol., ii, 30).—Whereas it is necessary by the German method, working at a pressure of 200 atmos., to pass the reacting gases over the catalyst a considerable number of times, with removal of the ammonia after each passage, it is only necessary to do this three times at a pressure of 1000 atmos. Other advantages of working at the higher pressure on an industrial scale are claimed. [See, further, *J. Soc. Chem. Ind.*, 1920, 187A.] W. G.

**Formation of Free Hydrogen in the Reversed Ammonia Flame.** FRIEDRICH U. G. MÜLLER (*Zeitsch. angew. Chem.*, 1920, **33**, 24).—The author finds that the products of combustion of ammonia in oxygen contain hydrogen and nitrogen in the ratio 2:3 by volume. Since the result is unaltered by cooling the flame with cold water (Raschig, A., 1919, ii, 148), it cannot be due to dissociation of ammonia. On the other hand, Raschig's assumption that the equation  $2\text{NH}_3 + \text{O}_2 = \text{N}_2\text{H}_2 + 2\text{H}_2\text{O}$  represents the first stage of the reaction, followed by instantaneous dissociation of  $\text{N}_2\text{H}_2$  and partial combustion of the hydrogen, does not account for the constancy of the proportion of hydrogen produced. J. K.

**The Velocity of Oxidation of Nitric Oxide.** EUGÈNE WOURTZEL (*Compt. rend.*, 1920, **170**, 229—231).—The oxidation of nitric oxide takes place according to the equation of a reaction of the third order, thus:  $-dp_{\text{NO}}/dt = k(p_{\text{NO}})^2 p_{\text{O}_3}$ .

The action does not undergo any marked modification when half the nitric oxide is oxidised; consequently, the exclusive and rapid

formation of nitrites or of nitrosyl sulphate observed, when the gaseous products formed at the commencement of the reaction are treated with alkali or sulphuric acid, must be due to particular conditions of absorption and not of oxidation of the nitric oxide. Nitrogen trioxide, the formation of which has previously been proved (compare next abstract), is an ulterior product of the action and not its intermediate product. The velocity of this oxidation diminishes with rise in temperature.

W. G.

### **The Existence of Nitrogen Trioxide in the Gaseous State.**

EUGÈNE WOURTZEL (*Compt. rend.*, 1920, **170**, 109—111. Compare this vol., ii, 108).—By measuring the contraction produced when known quantities of nitric oxide and oxygen are mixed, the nitric oxide being in excess, the authors have shown that under a total pressure of about one-quarter of an atmosphere an almost stoichiometric mixture of nitric oxide and nitrogen peroxide contains about 2.5% of nitrogen trioxide.

W. G.

### **Direct Formation of Carbon Monoxide by Burning Carbon in Pure Oxygen.**

FRIEDRICH C. G. MÜLLER (*Zeitsch. angew. Chem.*, 1920, **33**, 36).—If pure oxygen is passed downwards through a vertical quartz tube, 25 cm. in length and not more than 13 mm. in diameter, filled with pieces of wood charcoal of the size of linseed, the gas leaving the lower end of the tube will contain 85% of carbon monoxide. The upper part of the charcoal must be heated by a burner before the oxygen is admitted, and it is essential that the combustion is allowed to proceed under reduced pressure. This is attained by connecting the lower end of the tube with a vessel filled with water and opening the tap of the oxygen reservoir so that water flows from the lower vessel at the rate of 2 litres per minute.

W. P. S.

### **A Reaction of Potassium Anhydrotellurate.**

P. HULOT (*Bull. Soc. chim.*, 1920, [iv], **27**, 33).—If tellurous acid or alkali tellurites are brought to complete fusion with potassium nitrate, and the mass after cooling is extracted with water, potassium anhydrotellurate,  $K_2Te_4O_{13}$ , is left behind as a powder, which is insoluble in water or acids. If this powder is suspended in dilute hydrochloric acid and a few pieces of zinc are added, the salt gradually disappears and a black pulverulent powder, which is pure tellurium, is left behind.

W. G.

### **Application of the Reduction of Potassium Anhydrotellurate by Zinc to the Treatment of Tetradymite and to the Estimation of Tellurium in this Mineral.**

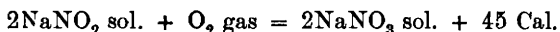
PIERRE HULOT (*Bull. Soc. chim.*, 1920, [iv], **27**, 100—101. Compare preceding abstract).—The tetradymite is first treated with dilute hydrochloric acid to remove the calcareous gangue. The powdered material is then dissolved in hot concentrated nitric acid, the solution being evaporated to dryness and the residue fused with twice its weight of potassium nitrate. The resulting mass contains potassium



sulphate and selenate, bismuth oxide, and potassium anhydrotellurate. The sulphate and selenate are removed with boiling water, and the residue is digested with dilute hydrochloric acid, whereby the bismuth oxide is dissolved out. The residue, after washing with dilute hydrochloric acid, is suspended in the same acid and some zinc is added. The whole of the tellurium is deposited in a pure state, and may be collected, dried, and weighed after the whole of the zinc has dissolved.

W. G.

**Reversible Oxidation of Sodium Nitrite.** C. MATIGNON and E. MONNET (*Compt. rend.*, 1920, **170**, 180—182).—Sodium nitrite, when heated in an atmosphere of oxygen at a pressure of 175 atmos. and at a temperature gradually rising from 395° to 530° during nine hours, is almost completely oxidised to sodium nitrate, the heat of formation of the nitrate being given by

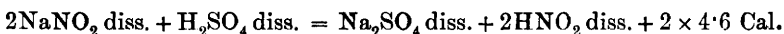


The reaction is too slow to be of practical use.

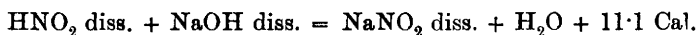
Calcium nitrite may similarly be converted into calcium nitrate.

W. G.

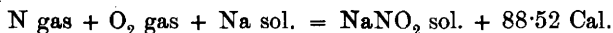
**Some Properties of Sodium Nitrite.** C. MATIGNON and (MLLE.) G. MARCHAL (*Compt. rend.*, 1920, **170**, 232—233).—The authors find for the m. p. of sodium nitrite 276·9° (corr.). Its heat of solution is expressed by  $\text{NaNO}_2 \text{ sol.} + \text{Aq} = \text{NaNO}_2 \text{ diss.} - 3\cdot52 \text{ Cal.}$  Its heat of decomposition in aqueous solution by dilute sulphuric acid is given by



From this equation and known data they deduce



and



Nitrous acid resembles nitric acid in its behaviour towards the following indicators: phenolphthalein, cochineal, litmus, *p*-nitrophenol, brazilin, and iodoeosin, but decomposes others, like helianthin.

Aqueous sodium nitrite is not oxidised at 100° by prolonged contact with oxygen under a pressure of 50—55 atmos., even in the presence of a catalyst.

W. G.

**Ammonium Silicate. III.** ROBERT SCHWARZ and RICHARD SOUARD (*Ber.*, 1920, **53**, [B], 1—17. Compare A., 1917, ii, 31; 1919, ii, 283).—The authors have studied the electrical conductivities of solutions of dioxodisiloxane, monosilane, and silicic acid obtained from pure and technical sodium silicate, silicon tetrachloride, and tetrafluoride in ammonia, in order to determine whether there are any indications of the existence of ammonium silicate or of different molecular complexity in silicic acid of various origins. The increment of the conductivity of ammonia solutions suggests that salt formation does take place, just as the lowering

of the conductivity of sodium hydroxide by silicic acid points to the same conclusion. The dialysis of the preparations and the technique of the measurements are described.

It was soon found that the percentage of water in the preparation had a great influence on the conductivity, partly due to the different rates at which the silicic acid entered real solution. In order to eliminate this factor, or to follow it more closely, the solutions were filtered through an ultra-filter after determining the conductivity, and the amount of silica estimated. The quotient, increment of conductivity/dissolved  $\text{SiO}_2$ ,  $\Delta k/m = Q$ , therefore affords a clue to the molecular complexity of the silicic acid. The experiments show that a decrease in the proportion of water in the dioxodisiloxane or silicic acid preparation is accompanied by a fall in the value  $Q$ , not, however, gradually, but apparently in three stages. In the case of dioxodisiloxane, the value  $Q$  is about 75 when the material contains about 4.5% of water, about 50 if the proportion of water is 2%, even though the silicic acid may imbibe more water on keeping, and about 25 if the preparation is almost dry. Similarly with the various silicic acid preparations; no matter what their origin, the nearly dry specimens give a value of about 25, and those rich in water about 75. After ignition, however, silica causes no increment in the conductivity of ammonia solutions. The different values of  $Q$  suggest, therefore, that the dissolved silicic acid exists in three forms, of molecular weights in the ratio 1:2:3. The simplest forms are derived from dioxodisiloxane or monosilane, the direct hydrolysis of the latter in ammonia solutions being the most satisfactory way of preparing ammonium silicate solutions.

J. C. W.

**Silver Peroxide and the Valency of Silver.** H. C. P. WEBER (*Trans. Amer. Electrochem. Soc.*, 1917, **32**, 391—404).—A number of experiments are described which were designed for the preparation of salts of silver in which the metal has a valency greater than unity. Except in the case of the peroxy-nitrate, the results were negative. This compound,  $2\text{Ag}_3\text{O}_4, \text{AgNO}_3$ , is formed on the anode during the electrolysis of silver nitrate, but if 15—25% of nitric acid is added to the solution there is no deposit, but a brown solution is formed. This solution, on examination, is found to contain both negative and positive silver-containing ions. The valency of the silver in the oxide portion of this salt is discussed. Two formulæ are put forward for the oxide part of the salt,  $\text{Ag}_3\text{AgO}_4$  (analogous to red lead) or  $\text{Ag}(\text{AgO}_2)_2$  (analogous to magnetic iron oxide). The transference experiments show that one-third of the silver is cathodic and bivalent and two-thirds anodic and tervalent, which leads to the formula  $\text{Ag}(\text{AgO}_2)_2$ . This indicates that the oxide portion of the peroxy-nitrate is the silver salt of an unstable *argentic acid*,  $\text{HAgO}_2$ .

J. F. S.

**Lead Borates.** H. V. THOMPSON (*Trans. Engl. Ceram. Soc.*, 1918—1919, **18**, 510—511).—The white precipitate formed by mix-

ing cold concentrated solutions of lead nitrate and borax is of indefinite composition, and does not necessarily consist of lead metaborate,  $\text{Pb}(\text{BO}_2)_2 \cdot \text{H}_2\text{O}$ , as stated by Rose (*Ann. Phys. Chem.*, 1833, **29**, 455). The precipitate formed by adding an excess of a solution of borax to a solution of a lead salt consists of lead metaborate, and not the polyborate,  $2\text{PbO} \cdot 3\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ , as stated by Soubeiran (*J. Pharm. Chim.*, 1825, **11**, 31).

On boiling the metaborate with an excess of boric acid solution, no definite chemical compound is formed, in contradiction to Abegg ("Handb. anorg. Chem.," 1909, **3**, ii), who states that the compound  $\text{PbO} \cdot 2\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  is produced.

The author confirms a statement by Le Chatelier (*Bull. Soc. chim.*, 1899, [iii], **21**, 35) that the compound  $\text{PbO} \cdot 3\text{B}_2\text{O}_3$  is formed on fusing boric acid and lead carbonate and extracting the mass with water to remove boric acid. [See also *J. Soc. Chem. Ind.* 1920, March.] A. B. S.

**Behaviour of Cerium Carbide towards Nitrogen.** FR. FICHTER and CHR. SCHÖLLY (*Helv. Chim. Acta*, 1920, **3**, 164—172).—The requisite finely divided cerium carbide is prepared by heating a mixture of cerium dioxide (1 mol.) and carbon (6 atoms) in a graphite tube in an electric vacuum-oven at  $1600^\circ$ . It is found that this material, in spite of its apparent similarity to calcium carbide, does not yield any compound with nitrogen at  $1250^\circ$  which contains both carbon and nitrogen, but that the carbon is replaced by nitrogen, with the formation of cerium nitride. The possibility of the formation of cyanides and cyanamides from carbides appears to exist solely in the groups of the alkali and alkaline earth metals, and not in that of the earthy metals; it does not depend on the type of the carbide, but on the nature of the metal. Cerium carbide also reacts with ammonia at  $1250^\circ$ , yielding the nitride, but the action is slower and less complete than when nitrogen is used. H. W.

**Some Complex Compounds of Mineral Chemistry.** G. URBAIN (*Bull. Soc. chim.*, 1920, [iv], **27**, 81—94).—A lecture delivered before the French Chemical Society W. G.

**Constitution of Ultramarine.** LAURENZ BOCK (*Zeitsch. angew. Chem.*, 1920, **33**, 23—24. Compare A., 1915, ii, 460; 1917, ii, 475).—Experiments on the action of ammoniacal silver chloride solution on artificial ultramarines are described. It is concluded that the blue rich in silica and sulphur, and based on the formula  $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ , is a definite chemical compound containing sodium, sulphur, aluminium, and silica in definite proportions; the same is true of the blue poor in silica but rich in sulphur. Further, the ultramarines are analogously constituted to the aluminium silicates. A table is given showing the known ultramarines and their relationship to natural and artificial silicates. J. K.

**Equilibrium in Blast Furnace Reactions.** ERNST TERRES and AUREL PONGRACZ (*Zeitsch. Elektrochem.*, 1919, **25**, 386—407).—The equilibrium of the reaction  $\text{Fe} + \text{CO}_2 \rightleftharpoons \text{FeO} + \text{CO}$  has been studied by a number of different observers, whose results show considerable divergencies. A fresh investigation has therefore been made on rather different experimental lines from those used hitherto. The reaction was studied from both sides, starting on the one hand from pure iron (iron wire or ferrum limatum) and carbon dioxide, and on the other from oxidised iron (prepared by oxidising pure iron with carbon dioxide) and carbon monoxide. The reaction was carried out in a pear-shaped glass vessel, which could be heated to any desired temperature in an electric furnace. For a full description of the special apparatus used, which embodied many devices for convenience and greater accuracy, the original must be consulted.

The usual procedure in studying such reactions as the one under consideration is to allow the reacting substances to remain in contact at the particular temperature until equilibrium is reached, and then to analyse the products. This method was used by Baur and Glaessner (A., 1903, ii, 423), who plotted the composition of the gases at the end of the reaction against the temperature and obtained two distinct curves, the one obtained from the starting materials, iron and carbon dioxide, having a well-marked minimum, and the other, from ferroso-ferric oxide and carbon monoxide, showing an equally prominent maximum. The present authors allowed the reaction to proceed for a definite time at each particular temperature, and at the end of this time the gases were analysed. The reaction was studied over the temperature range  $550^\circ$  to  $950^\circ$ . The results are plotted in the form of four curves, two showing the composition of the gas mixture after seven hours, starting from either side of the equation, the other two after sixteen hours. Each curve is a straight line, the proportion of carbon monoxide in the mixed gases increasing steadily with the temperature. All four curves converge towards a point at about  $950^\circ$  with about 75% of carbon monoxide, showing that in seven hours equilibrium is already attained at this temperature. The two sixteen-hour curves lie between the seven-hour curves, quite close together, and converge at about  $810^\circ$ , showing that at this temperature equilibrium is reached in sixteen hours. The true equilibrium curve evidently lies about midway between the two sixteen-hour curves. Contrary to the results of Baur and Glaessner, the same equilibrium point is reached from either side of the equation, and the curve shows no maximum or minimum. These results are in agreement with those obtained by Schenck and his co-workers (A., 1903, ii, 423; 1905, ii, 526; 1907, ii, 470) and by Levin (A., 1912, ii, 1176).

Very careful experiments showed that the composition of the gas phase at equilibrium depends on the quantity of the solid phase present, the proportion of carbon monoxide increasing with increasing amounts of iron. This can be explained on the assump-

tion that the ferrous oxide phase is a solid solution of two components. A method for analysing the solid phase was devised, and it was shown that this always contained ferric iron. The proportion of ferrous to ferric oxide never corresponded with the composition  $\text{Fe}_3\text{O}_4$ . It was also shown that no other constituent was present in the solid phase. The fall in pressure always observed when carbon dioxide and iron are first heated together is due, not to any chemical reaction, but to absorption of the gas by the metal. [See also *J. Soc. Chem. Ind.*, 1920, 193A.] E. H. R.

**Behaviour of Iron in Contact with Sulphuric Acid.** C. E. FAWSITT and A. A. PAIN (*J. Proc. Roy. Soc. N.S. Wales*, 1918, **52**, 396—405).—Differences in electrochemical behaviour show that no real similarity exists between iron which is slowly dissolving in concentrated sulphuric acid and iron rendered "passive" by dipping into nitric acid. The slowing down or cessation of the reaction is due apparently to the formation of a form of ferrous sulphate monohydrate on the surface of the iron. Although, generally speaking, increased dilution of the acid with water results in greater reactivity, certain anomalies were observed in this respect, notably that 89.3% acid has considerably less solvent action than either weaker or stronger acid of 94%, 90.9%, 87.9%, or 85% strength. The solvent effect is in all cases noticeably increased by shaking the containing vessel. G. F. M.

**The Critical Points of Self-hardening Steels.** P. DEJEAN (*Compt. rend.*, 1919, **169**, 1043—1045).—It has previously been shown (A., 1917, ii, 477), that there is a distinct discontinuity between the formation of perlite or troostite and martensite, the critical point corresponding with the formation of the former being "A" and of the latter "B." It is now noted from a study of the cooling curves of a nickel-chrome-copper steel, which, starting from different initial temperatures, was cooled from  $700^\circ$  to  $100^\circ$  in about one hundred and fifty minutes, that the formation of martensite apparently occurs in two stages denoted by critical points  $B_1$  and  $B_2$ . The point A is indicated only when the critical temperature of cooling is  $790^\circ$ . When this temperature rises to  $800^\circ$ , A is considerably suppressed and the critical point  $B_1$  appears at about  $420^\circ$ . If the steel is cooled from  $850^\circ$  the second point  $B_2$  occurs at about  $230^\circ$ , and if cooled from still higher temperatures  $B_1$  disappears and the point  $B_2$  exists alone. If only the point A is in evidence during cooling the steel is relatively soft, but becomes harder when  $B_1$  predominates and still harder when  $B_2$  appears. It is concluded that for the steel studied the maximum hardness is reached in at least two stages, and that for the same steel there may be several martensitic forms. W. G.

**The Formula of Chromium Hydroxide.** MIL. Z. JOVITSCHITSCH (*Helv. Chim. Acta*, 1920, **3**, 46—49).—The solubility of chromium hydroxide in ammonia and the preparation from such solutions of complex salts which invariably contain  $10\text{H}_2\text{O}$  (compare

A., 1913, ii, 223) leads the author to assign the formula  $\text{Cr}_4(\text{OH})_8\text{O}_2 \cdot 10\text{H}_2\text{O}$  or  $\text{Cr}_4(\text{OH})_{10}\text{O} \cdot 9\text{H}_2\text{O}$  to chromium hydroxide. Stronger evidence in favour of such formulation is found in the absorption of carbon dioxide from the air by chromium hydroxide with the formation of a carbonate,  $\text{CO}_3 \cdot 2\text{Cr}_2(\text{OH})_6 \cdot 8\text{H}_2\text{O}$ , to which the formula  $\text{Cr}_2(\text{OH})_6 \cdot \text{O} > \text{CO} \cdot 9\text{H}_2\text{O}$  or  $\text{O} < \text{Cr}_2(\text{OH})_4 \cdot \text{O} > \text{CO} \cdot 10\text{H}_2\text{O}$  is ascribed (compare A., 1914, ii, 373). H. W.

**Chromium Chromate,  $\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ .** MIL. Z. JOVITSCHITSCH (*Helv. Chim. Acta*, 1920, 3, 40–46).—When a solution of chromium oxide in nitric acid (compare A., 1912, ii, 261) is evaporated until excess of acid is removed and the residue is dissolved in water and treated with ammonia, a dark brown, almost black product is obtained, analyses of which are in agreement with the formula  $\text{Cr}_2(\text{OH})_8 \cdot \text{H}_2\text{O}$  or  $\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ . The loss of  $1\text{H}_2\text{O}$  over sulphuric acid, of  $2\text{H}_2\text{O}$  at  $105^\circ$ , and of  $6\text{H}_2\text{O}$  at  $205^\circ$  is more readily explained by the former, but the chromium content and particularly the possibility of the preparation of anhydrous chromium chromate from the substance, lead the author to give preference to the latter. The substance is somewhat unstable and loses chromium trioxide when repeatedly washed even with warm water. It forms a very suitable initial material for the preparation of pure chromium hydroxide free from alkali, which is effected by boiling a solution of the substance in concentrated hydrochloric acid with alcohol until reduction is complete and subsequently adding ammonia in excess.

Anhydrous chromium chromate cannot be prepared by heating the hydrated product, since decomposition occurs before the last molecule of water is removed; it may, however, be obtained as a porous, black mass by dissolving chromium oxide in nitric acid, evaporating the solution to dryness, and cautiously heating the residue to  $290^\circ$ . The analytical data agree equally well with those required for the peroxide,  $\text{CrO}_2$ , but the readiness with which the substance is converted by ammonia, alkali carbonate, or hydroxide or by boiling water into chromium hydroxide and chromate is interpreted in favour of a salt-like constitution. H. W.

**Electro-deposition of Nickel.** L. D. HAMMOND (*Trans. Amer. Electrochem. Soc.*, 1916, 30, 103–134).—The best conditions for securing a satisfactory anode corrosion in the electro-deposition have been sought by studying the polarisation pressures and the current efficiency obtained with anodes of cast nickel, electrolytic nickel, and annealed nickel in solutions of nickel sulphate containing measured amounts of boric acid and nickel chloride. The experiments show that although cast nickel anodes corrode fairly well in simple sulphate solutions to which boric acid has been added, the best results are obtained when the purest electrolytic nickel in nickel sulphate solutions containing chloride is used. Nickel chloride is to be preferred to other chlorides, as its addition does

not decrease the concentration of nickel in the electrolyte. It is shown that 6 grams of nickel chloride per litre produce a good anode corrosion, and that the best results are secured by increasing the concentration of nickel chloride to 15 grams per litre. The conditions necessary for the direct electro-deposition of nickel on zinc have been investigated. It is shown that nickel can be directly deposited on zinc from the baths used to deposit nickel on more electro-negative metals if a higher initial current density is employed than is usual when using these baths for their ordinary purposes. An electrolyte consisting of 120 grams of nickel sulphate, 15 grams of nickel chloride, 30 grams of boric acid, and 1000 c.c. of water may be used to deposit nickel on zinc, copper, brass or iron. To deposit on copper a current density varying from a few tenths of an ampere to 3 or 4 amperes may be used, but to deposit on zinc a current density of not less than 3 amperes must be employed. It is suggested that whilst the above-named bath produces good deposits on flat strips of zinc, it will probably give a deposit with black streaks if irregular objects are to be plated. The following bath composition, however, produces perfect deposits on irregular objects: 240 grams of nickel sulphate, 15 grams of nickel chloride, 30 grams of boric acid, 175 grams of sodium citrate, and 1000 c.c. of water. This bath gives good deposits with current densities 0.5—7 amperes per sq. dcm. if pure nickel anodes are used. The two baths named are very rapid in their action. Nickel has been deposited directly on zinc from a  $N/2$ -solution of hydrochloric acid containing 120 grams of nickel sulphate per litre. Sodium citrate has a beneficial effect on baths for the direct nickeling of zinc, which is not due to a change in the potential of zinc, but to a decrease in the rate of deposition by immersion. Sodium potassium tartrate and sodium malate have a similar action, but they do not permit the use of so high a current density as the citrate bath. The substitution of nickel ammonium sulphate by nickel sulphate in nickeling baths is recommended. To ensure a good deposit of nickel it is essential that the bath should be slightly acid, and it is for this purpose that boric acid is added. The function of the boric acid is therefore to maintain a small but fairly constant concentration of hydrogen ions in the electrolyte.

J. F. S.

**Isolation of Molybdenum and working up of Molybdenum Residues.** S. MALOWAN (*Chem. Zeit.*, 1918, 42, 410).—To recover molybdic acid used as a precipitant in phosphorus determinations, the liquor is precipitated with sodium or calcium phosphate. The yellow precipitate, after being washed and dried, is heated with excess of concentrated sulphuric acid until solution is complete and the acid colourless. The cold liquid is poured into eight to ten times its volume of water, and the molybdenum precipitated with excess of ferrocyanide. The precipitate is collected after three hours, washed with dilute ferrocyanide solution until all the acid is removed, dried, separated from the paper, and ignited at a dark red heat to incipient fusion. The cooled product is leached

twice with hot water, then extracted with ammonia, which dissolves molybdic acid. The colourless solution is filtered, evaporated to dryness, the residue dissolved in a little water and hydrogen peroxide, and the solution boiled to oxidise any lower oxides. The resulting solution of ammonium molybdate is diluted until it has  $D^{17} 1.09$  (that is, 10 per cent.).

W. R. S.

**Reversible Reaction of Water on Molybdenum.** GEORGES CHAUDRON (*Compt. rend.*, 1920, **170**, 182—185).—A study of the system water vapour-molybdenum-hydrogen-molybdenum dioxide over the temperature range  $700-1100^{\circ}$ . The values of  $K = p_{H_2O}/p_{H_2}$  obtained by the oxidation of the metal or the reduction of the oxide agree closely. Plotting  $\log K$  against  $1/T$ , the points obtained lie on a straight line within the temperature interval considered.

W. G.

**The Violet Compounds of Uranium.** J. ALOY and E. RODIER (*Bull. Soc. chim.*, 1920, [iv], **27**, 101—105).—The production of violet compounds of uranium as described by Aloy (compare A., 1901, ii, 317) is not an exceptional phenomenon, but quite general, and does not necessarily involve the action of light. It is necessary to distinguish between salts of inorganic acids and salts of organic acids. Salts of the first type must be used in exactly neutral solution and in the presence of a readily oxidisable substance. Both violet and ultra-violet rays cause the production of violet precipitates, the ultra-violet rays being the more active. The action of light is not always necessary, and it is shown that these violet compounds are obtained whenever a uranous and a uranic salt are present together at the requisite temperature in a neutral or feebly acid medium.

In reality, there exist a large number of violet compounds of uranium, having an analogous constitution, all of which, by loss of their acid radicles, tend to become transformed into the green, hydrated oxide,  $U_3O_8 \cdot 2H_2O$ .

W. G.

**Soluble Metastannic Acid.** HANS KREIS (*Schweiz. Chem. Zeit.*, 1919, 389).—Spongy tin is dissolved in a solution of ferric nitrate in nitric acid,  $D 1.23$ , and, after the vigorous reaction has subsided, hot water is added. The resulting, slightly opalescent solution contains colloidal metastannic acid, and may be repeatedly evaporated to dryness, with or without addition of more nitric acid, without precipitation of the tin (compare Antony and Mondolfo, A., 1899, ii, 330). The author considers that the ferric hydroxide formed by dissociation of the ferric nitrate acts as a protective colloid.

A. R. P.

**The Question of the Existence of Zirconium Monoxide.** R. SCHWARZ and H. DEISLER (*Ber.*, 1920, **53**, [B], 1. Compare this vol., ii, 42).—A recognition of similar work by Wedekind (A., 1913, ii, 225).

J. C. W.



**Electrolysis of Aqueous Solutions of Vanadium Salts.**

SIEGFRIED FISCHER, jun. (*Trans. Amer. Electrochem. Soc.*, 1916, **30**, 175—228).—Several hundred experiments are described in tabular form, which have been made with the object of depositing metallic vanadium from aqueous solutions. After a resumé of the literature of the deposition of vanadium, the author describes fifty-five experiments made with Cowper-Coles vanadium electrolyte (1.75 vanadium pentoxide, 2.00 sodium hydroxide, 160.0 water, and after boiling 32.0 hydrochloric acid) (A., 1899, ii, 755). It is found that in no circumstances can metallic vanadium be obtained from this electrolyte. The reduction of the electrolyte is limited in most cases to the vanadyl state, which is blue ( $V_2O_4$ ). A reduction occurs in practically all the experiments. At temperatures of  $90^\circ$  or above, the reduction may be taken to the lavender colour ( $V_2O_3$ ). Lead electrodes alone give a reduction to the sesquioxide ( $V_2O_3$ ), or green state, at temperatures below  $90^\circ$ ; above  $90^\circ$  the electrolyte is reduced to the lavender state. Carbon electrodes reduce the electrolyte to the green state. At temperatures below  $90^\circ$  platinum electrodes reduce the electrolyte to the blue vanadyl state only, and the current density has no influence on this. At temperatures above  $90^\circ$  the lavender state is reached only when porous cells are used. The black deposit obtained by Cowper-Coles on platinum electrodes is not a vanadium compound, but platinum hydride. A number of experiments (112) were made with solutions of vanadium pentoxide in sulphuric acid in the presence of various concentrations of aluminium sulphate, magnesium sulphate, ammonium sulphate, hydrofluoric acid, boric acid, or silicic acid, using electrodes of platinum, carbon, lead, and mercury. When platinum electrodes were used a black film was obtained, which contained no vanadium. In no case was metallic vanadium obtained. Solutions of vanadic acid in hydrochloric acid, sulphuric acid, nitric acid, hydrofluoric acid, lactic acid, ethyl hydrogen sulphate, and tartaric acid were electrolysed, as well as a series of solutions of vanadic oxide in alkali hydroxide, but in no case could metallic vanadium be obtained. The reason for the failure to obtain metallic vanadium is the very large heat of formation of vanadium salts. Thus the oxide  $V_2O_5$  has a heat of formation 441000 cal.;  $V_2O_3$ , 353200 cal.; VO, 104300 cal. J. F. S.

**Formation and Nature of Black Antimony Trisulphide.**

FERRUCCIO DE BACHO (*Annali Chim. Appl.*, 1919, **12**, 143—152).—On heating red antimony trisulphide in carbon dioxide, there is no material difference in the loss of weight at temperatures from  $150^\circ$  to  $300^\circ$ , the change to the black modification taking place at  $212^\circ$ , whilst in a current of hydrogen sulphide the change occurs at  $207^\circ$ . By adding ammonium chloride to the red sulphide, the temperature of the change in carbon dioxide is lowered (for example, to  $170^\circ$ ), whilst the presence of antimony chloride reduces the temperature still further. Thus in the case of a mixture of equal parts of antimony trisulphide and trichloride, the black

coloration appeared at 125°. Metallic silver also has a favourable influence on the transformation. The action of ammonium chloride in boiling solution also promotes the formation of the black sulphide to an extent depending on the concentration of the solution, whilst the rapidity of the transformation stands in relationship to the degree of hydrolysis of the ammonium chloride, and consequent acidity of the solution. The presence of antimony trichloride facilitates this conversion, which is accelerated by the presence of hydrochloric acid, antimony trisulphide, and potassium nitrate at high concentrations. Concentrated solutions of electrolytes, such as sodium chloride, ammonium sulphate, or potassium nitrate alone have no effect on the transformation, which is therefore not merely the result of molecular condensation. The conversion always takes place when the conditions permit of immediate contact between the red antimony trisulphide and antimony trichloride, whether added as such or formed in the solution. It is probable that the following reaction takes place:  $2\text{Sb}_2\text{S}_3 + 2\text{SbCl}_3 \rightarrow 6\text{Sb} + 3\text{S}_2\text{Cl}_2$ . It is also probable that the trace of free antimony thus formed, or that produced by dissociation of the red trisulphide when heated, forms in the colloidal condition a solid solution with the antimony trisulphide. This decomposition, which occurs in the process of drying in analytical work, is too small to be detected gravimetrically. On heating the red trisulphide, there is a gradual increase in the specific gravity, but the conversion into the black modification is not indicated by any sudden rise in the specific gravity.

C. A. M.

**The Action of Aqua Regia on Gold-Silver Alloys in the Presence of Ammonium Salts.** WILLIAM BRANCH POLLARD (T., 1920, 117, 99—103).

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### Mineralogical Chemistry.

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**Colloid Colour Substances in Minerals.** C. DOELTER (*Kolloid Zeitsch.*, 1920, **26**, 23—27).—A theoretical paper in which it is shown that the colours of many minerals are due to small quantities of impurities, which may be the same in differently coloured minerals. The nature of the colour depends on the size of the particles of the pigment. Change in the colour effected by heating or by the action of radium rays is due to a change in the dimensions of the particles. J. F. S.

**A Markedly Ceritic Fluorapatite from Latium.** I. BELLUCCI and L. GRASSI (*Gazzetta*, 1919, **49**, ii, 232—246).—A nodule included in the building stone known as “peperino,” occurring in a cave in the Ariccia district, is found to consist principally of olivine and biotite, together with numerous small, shining, crystalline aggregates having a radiating, fibrous structure and a pale emerald-green colour. This green mineral, D 3·23—3·29,

$n$  1.63—1.65, is a fluoapatite containing comparatively large proportions of rare earths; analysis gave:

CaO.	Rare earth oxides.	FeO.	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	F.	Total.
50.86	5.24	1.92	35.5	2.59	3.37	99.48

The rare earths present are ceritic and not yttric in character, the presence of cerium, didymium, and lanthanum being demonstrated.

A summary is given of the literature dealing with apatites containing rare earths. In the apatite of Narsarsuk, Flink (A., 1900, ii, 410) found 3.36% of yttric oxides and 1.52% of ceritic oxides.

T. H. P.

### The Origin of the Beds of Sodium Carbonate in Peru.

EMM. POZZI-ESCOT (*Bull. Soc. chim.*, 1919, [iv], 25, 614—617).—It is suggested that the sodium sulphate of the soil dissolves in the water which gradually collects in natural depressions, forming salt marshes, with an abundance of vegetation suited to the conditions. The sulphate in contact with the plants and algæ becomes reduced to sulphide, which is then in its turn decomposed by carbon dioxide, either atmospheric or that resulting from local vegetative combustion, with the resulting formation of sodium carbonate or sodium hydrogen carbonate. The industrial possibilities of these deposits are discussed.

W. G.

**Mineralogy of Sweden.** GUST. FLINK (*Arkiv Kemi Min. Geol.*, 1917, 6, No. 21, 1—149).—In Part IV of his "Mineralogy of Sweden," the author gives detailed descriptions of forty-five

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	PbO.	GfO.
I.....	16.61	—	—	—	77.63	—
II.....	16.50	—	—	—	77.70	—
III.....	17.74	—	—	—	66.53	—
IV.....	17.21	—	—	—	70.14	—
V.....	39.84	—	—	0.15	—	16.53
VI.....	40.00	—	—	trace	—	11.49
VII.....	37.53	23.79	7.73	3.85	—	—
VIII.....	45.53	23.07	1.93	—	—	—
IX.....	43.54	22.62	1.79	—	—	—
X.....	43.40	23.05	1.27	—	—	—

	MnO.	CaO.	MgO.	H <sub>2</sub> O.	Total.	Sp. gr.
I.....	0.35	1.75	0.41	0.40	99.95*	6.53
II.....	2.83	0.52	0.10	0.08	99.82†	6.706
III.....	2.88	10.42	0.45	0.60	99.11‡	5.576
IV.....	2.78	7.31	0.95	—	98.39§	—
V.....	26.82	15.67	0.55	0.54	100.10	3.404
VI.....	7.05	37.82	0.94	2.48	99.93	3.16
VII.....	0.48	21.97	0.34	3.14	99.63**	3.189
VIII.....	—	25.48	—	4.48	100.49	—
IX.....	—	26.56	—	4.81	99.32	2.914
X.....	trace	26.49	0.40	4.89	99.50	2.906

\* Including Fe 0.10, Cl trace.

† Including ZnO 0.90, K<sub>2</sub>O 0.09, Na<sub>2</sub>O 0.40, SO<sub>3</sub> 0.63, Cl 0.12.

‡ Including Na<sub>2</sub>O 0.06, K<sub>2</sub>O 0.17, CO<sub>2</sub> 0.26.

§ Including Cl 0.10.

|| Including F 0.15.

\*\* Including TiO<sub>2</sub> 0.11, K<sub>2</sub>O 0.24, Na<sub>2</sub>O 0.45.

species belonging to the silicate group. Analyses are given of the following: I and II, barysilite of different types from Jakobsberg; formula,  $Pb_3Si_2O_7$ . Ganomalite, III, from Jakobsberg, IV from Långban. V, trimerite from Jakobsberg; formula,  $Gl_2SiO_4 \cdot (Mn, Ca)_2SiO_4$ . VI, harstigitite from Harstig mine; formula,  $Gl_2Ca_3Si_3O_{11}$ . VII, epidote from Nols felspar quarry, Göta. Prehnite, VIII from Uppsala district, IX from Hästberg estate, near Falun, X from Sjösa iron mine, near Svärta.

L. J. S.

**Presence of Lithium in the Salts of Vesuvian Fumaroles.**

L. DE LUISE (*Gazzetta*, 1919, **49**, ii, 328—329).—The salts from the fumaroles of the crater of Vesuvius have the composition: potassium chloride, 20·521%; sodium chloride, 79·458%; iron and aluminium, traces. Sometimes lithium is present in small proportion, and in one instance 180 grams of the mixed chlorides were found to contain lithium chloride corresponding with 0·07 gram of lithium sulphate.

T. H. P.

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### Analytical Chemistry.

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#### Qualitative Analysis in the Presence of Phosphoric Acid.

HEINRICH REMY (*Zeitsch. anal. Chem.*, 1919, **58**, 385—392).—The following procedure is recommended for the qualitative analysis of a solution containing various metals, etc., and phosphoric acid. Heavy metals are first separated by means of hydrogen sulphide; the filtrate from the sulphide precipitate is boiled to expel hydrogen sulphide, filtered, heated with the addition of a small quantity of nitric acid, then nearly neutralised with ammonium carbonate, treated with an equal volume of concentrated ammonia, and an excess of ammonium phosphate is added. Aluminium, chromium, iron, calcium, strontium, barium, manganese, and magnesium are precipitated, whilst zinc, nickel, cobalt, and alkali metals remain in solution. The precipitate is dissolved in warm dilute hydrochloric acid, potassium sulphate solution is added, and the precipitated alkali earth sulphates are collected on a filter and separated and identified in the usual way. The filtrate from the sulphates is boiled with the addition of sodium acetate and ammonium chloride; iron, chromium, manganese, and aluminium are precipitated, whilst magnesium and a small quantity of calcium remain in solution. The precipitate is dissolved in hydrochloric acid, boiled, nearly neutralised with sodium carbonate, and then poured into a mixture of hydrogen peroxide and 20% sodium hydroxide solution. Iron and manganese are precipitated, whilst chromium and aluminium are converted into soluble chromate and aluminate respectively. The filtrate from the first phosphate precipitate, and

containing the zinc, etc., is heated, treated with ammonium sulphide, the precipitate is collected (the filtrate from this precipitate contains the alkali metals), and the zinc sulphide is dissolved in dilute hydrochloric acid, in which nickel sulphide and cobalt sulphide are insoluble. The hydrochloric acid solution is then rendered strongly alkaline with sodium hydroxide, heated, diluted, and filtered; zinc is precipitated from the filtrate as sulphide after the addition of acetic acid. Nickel and cobalt are separated and identified in the usual way.

W. P. S.

**Method of Stating Analytical Results.** A. THIEL (*Chem. Zeit.*, 1920, **44**, 81—82).—A discussion advocating the use of equivalent units in expressing the results of analysis.

W. P. S.

**Influence of Temperature on the Strength of Standard Solutions in Quantitative Analysis.** YUKICHI OSAKA (*J. Tokyo Chem. Soc.*, 1919, **40**, 424—449).—The tables previously published (*ibid.*, 1911, **32**, 450) showing the changes in the concentration of standard solutions at different temperatures, taking 15° as the standard temperature, have been extended for temperatures from 5° to 30°, each being compared with three standards, at 15°, 20°, and 25°. Nineteen tables are given for *N*- and *N*/10-oxalic acid, *N*-hydrochloric, nitric, and sulphuric acids, *N*- and *N*/10-sodium carbonate, *N*/10-sodium hydroxide, *N*/10- and *N*/100-sodium chloride, *N*/10- and *N*/100-silver nitrate, *N*/10- and *N*/100-potassium permanganate, *N*/10-ammonium thiocyanate, and water. The change in the concentration of the solution and in the volume of the flask produced at different temperatures is recorded. The results are summarised in the following table:

Standard temp. :	15°.		20°.		25°.	
Solution temp. :	5°.	30°.	5°.	30°.	5°.	30°.
NaOH ( <i>N</i> ) .....	1.00245	0.99508	1.00393	0.99655	1.00559	0.99819
Na <sub>2</sub> CO <sub>3</sub> ( <i>N</i> ) .....	1.00230	0.99521	1.00374	0.99664	1.00534	0.99820
HNO <sub>3</sub> ( <i>N</i> ) .....	1.00227	0.99516	1.00371	0.99658	1.00534	0.99822
H <sub>2</sub> SO <sub>4</sub> ( <i>N</i> ) .....	1.00231	0.99516	1.00365	0.99659	1.00526	0.99818
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ( <i>N</i> ) .....	1.00160	0.99580	1.00279	0.99698	1.00422	0.99840
HCl ( <i>N</i> ) .....	1.00153	0.99608	1.00264	0.99718	1.00395	0.99849
NaCl (0.1 <i>N</i> ) .....	1.00108	0.99642	1.00201	0.99735	1.00321	0.99854
AgNO <sub>3</sub> (0.1 <i>N</i> ) .....	1.00105	0.99640	1.00202	0.99737	1.00321	0.99856
NH <sub>4</sub> CNS (0.1 <i>N</i> ) .....	1.00104	0.99639	1.00199	0.99734	1.00322	0.99856
KMnO <sub>4</sub> (0.1 <i>N</i> ) .....	1.00096	0.99643	1.00193	0.99737	1.00312	0.99856
Na <sub>2</sub> CO <sub>3</sub> (0.1 <i>N</i> ) .....	1.00095	0.99675	1.00177	0.99757	1.00287	0.99866
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> (0.1 <i>N</i> ) .....	1.00078	0.99674	1.00161	0.99757	1.00270	0.99866
NaCl (0.01 <i>N</i> ) .....	1.00089	0.99649	1.00178	0.99738	1.00295	0.99853
AgNO <sub>3</sub> (0.01 <i>N</i> ) .....	1.00089	0.99655	1.00177	0.99743	1.00294	0.99858
KMnO <sub>4</sub> (0.01 <i>N</i> ) .....	1.00087	0.99653	1.00181	0.99745	1.00294	0.99858
H <sub>2</sub> O .....	1.00083	0.99661	1.00174	0.99751	1.00288	0.99864

The average from all equinormal solutions is given in the final table for each temperature from 5° to 30° against three standard temperatures. This table could be used for any *N*-solution, within error of 5 in 10,000. Another table is given which could be applied for any solution less than 0.1*N* within error of 5 in 10,000. It is

pointed out that maximal errors for two solutions of equal strength made at two extreme temperatures ( $5^{\circ}$  and  $30^{\circ}$ ) is 7:1000 for  $N$  and 5:1000 for solutions less than  $0.1N$ .

#### CHEMICAL ABSTRACTS.

**The Effect of a Change in Temperature on the Colour Changes of Methyl-orange, and on the Accuracy of Titrations.** HENRY THOMAS TIZARD and JOHN REGINALD HARVEY WHISTON (T., 1920, 117, 150—156).

**Indicator Papers.** D. J. DE JONG (*Pharm. Weekblad*, 1919, 56, 465—467).—An extension and amplification of previous communications (*ibid.*, 179, 238, 328, 404, 405). If a drop of acid is placed on ordinary filter paper and tested with methyl-orange, a weak reaction will be indicated in a ring surrounding the drop, and beyond this will exist a neutral "water ring." If the paper is previously treated with hydrogen chloride, washed, and dried, it becomes saturated with hydrogen ions, and further absorption of these from the drop will be prevented. A stronger coloration will thus result, and will be produced in the whole moistened portion. Addition of acid to methylene-blue similarly increases its sensitiveness.

W. J. W.

**Use of the Electrometer for Titrations.** J. PINKHOFF (*Pharm. Weekblad*, 1919, 56, 1218—1234).—The author gives a description of the apparatus and mode of operation in carrying out titrations by the potential method. A difference of potential of 1 millivolt should be detected by a suitable electrometer. The scope of the method and its special applications are discussed at some length.

W. J. W.

**Use of Arsenious Anhydride in Namias' Method of Volumetric Analysis.** FERRUCCIO DE BACHO (*Annali Chim. Appl.*, 1919, 12, 136—142).—In Namias's method (A., 1892, 1374) any given oxidising agent is treated with an excess of arsenious anhydride in the presence of ammonium acetate, and the boiling liquid titrated with iodine solution after the addition of acetic acid. Critical experiments have shown that this method is untrustworthy. No blue coloration is given by starch paste with iodine at  $60^{\circ}$ — $70^{\circ}$ , and it is therefore useless to employ it as an indicator in a boiling solution. The presence of ammonium chloride formed from the ammonium acetate when the solution contained hydrochloric acid also influences the results. Equilibrium between the reacting substances is then only very slowly attained. Contrary to the assertion of Namias, the reaction between arsenious anhydride and chromic acid is only complete after prolonged action, and the results obtained are invariably too high and not concordant.

C. A. M.

**New Volumetric Reduction Method with Arsenious Anhydride.** FERRUCCIO DE BACHO (*Annali Chim. Appl.*, 1919, 12, 153—174).—An oxidising agent is treated with excess of arsenious



acid solution in the presence of hydrochloric acid, and the solution subsequently titrated with standard potassium bromate solution, methyl-orange being used as indicator. To prevent loss through volatilisation of arsenic chloride the proportion of hydrochloric acid must not exceed 12·8%, a distinct loss occurring when it reaches 15%. In many cases the reduction is complete at the ordinary temperature, but as a rule it is preferable to boil the liquid beneath a reflux condenser. The method gives good results in the analysis of permanganates, in the estimation of manganese dioxide in pyrolusite, and the analysis of chlorates and chromates, including lead chromate. In the case of mixtures of hypochlorites and chlorates the hydrochloric acid is reduced to 5% to retard the action of the chlorate during the estimation of the hypochlorites. The acid is then increased to 12% and the reduction effected at boiling point, when both chlorates and hypochlorites react, and the amount of the former is found by difference. [See, also, *J. Soc. Chem. Ind.*, 1920, March.]  
C. A. M.

**Improved Electro-analysis Apparatus.** J. L. JONES (*Trans. Amer. Electrochem. Soc.*, 1917, **32**, 329—334).—A description of a six- and a ten-unit electrically stirred electrolytic apparatus for the quantitative analysis of non-ferrous alloys. The electrodes and beakers are fixed; stirring is effected by revolving tungsten rods. Each electrolysis receives a separate current which may be varied between 0·5 and 6·0 amps. A switch and push-button before each unit enable the current and *E.M.F.* to be read at any moment.

J. F. S.

**Use of Lead as a Substitute for Platinum in Analysis.** CARL HÜTTER (*Zeitsch. angew. Chem.*, 1919, **32**, 380).—Platinum basins may be replaced by lead basins for certain quantitative estimations. Thus in the case of chrome iron ore the mineral may be heated with concentrated sulphuric acid in a lead basin on the water-bath, and any lead sulphate formed removed without interfering with the subsequent analysis. The method is suitable for the estimation of silicon, aluminium, potassium, and sodium, for which silica or silver basins cannot be used. Any alteration in the stage of oxidation is prevented by introducing a current of carbon dioxide through a porcelain tube inserted into a hole in the middle of the lead cover of the basin.  
C. A. M.

**Catalytic Reduction of Organic Halogen Compounds.** M. BUSCH (*Zeitsch. angew. Chem.*, 1918, **31**, 232).—In the catalytic reduction of organic halogen compounds by means of palladium, hydrazine may be substituted with advantage for a current of purified hydrogen. 0·2 Gram of the organic compound is dissolved in 40—50 c.c. of alcohol; 2 grams of palladinised calcium carbonate, or barium sulphate, 2·5 c.c. of 50% potassium hydroxide, and 10 drops of hydrazine hydrate are added. The liquid is boiled under reflux for thirty minutes, after which the bulk of the alcohol

is expelled on the water-bath. The catalyst is filtered off, and the halogen determined in the filtrate after acidification with nitric acid.

W. R. S.

**Estimation of Organic Chlorine or Bromine by the Chromic Acid Method.** P. W. ROBERTSON (*Chem. News*, 1920, 120, 54).—To overcome minor difficulties encountered in the chromic acid method of estimating organic chlorine or bromine (T., 1915, 107, 902), the following modifications are suggested. A freshly prepared cold solution of sodium peroxide is used as absorbing medium instead of sodium hydroxide solution containing hydrogen peroxide. The chromic anhydride may be replaced by halogen-free potassium dichromate, and  $N/20$ -solutions of silver nitrate and ammonium thiocyanate are recommended instead of  $N/10$ -solutions. Finally, in the case of compounds, particularly liquids, which react explosively with the oxidising mixture, the best procedure is to cover the substance with a large amount of powdered dichromate and run the previously cooled sulphuric acid very rapidly into the reaction vessel through a wide funnel by means of a suction pump connected with the absorption tube. The reaction vessel is cooled in ice until the initial violence of the oxidation has moderated.

G. F. M.

**Iodometric Estimation of Chloric Acid.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, 56, 460—465).—The direct iodometric estimation of chlorate in a strongly acid medium gives high results owing to oxidation of hydrogen iodide by atmospheric oxygen. Rupp's method (A., 1918, ii, 125) is satisfactory. It is sufficient, however, to use hydrochloric acid to the extent of one and a-half times the volume of the chlorate solution, and only 100 c.c. of potassium iodide need be added. By using ferrous sulphate, still smaller quantities of reagents may be employed. The chlorate solution is boiled with 10 c.c. of 4*N*-hydrochloric acid and ferrous sulphate; 1 gram of potassium iodide is added at 50°, and the solution then titrated with slight heating towards the end.

W. J. W.

**Estimation of Iodide.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, 56, 1029—1035).—Estimations were made by several known methods with the same preparation of potassium iodide (0.098*N*) in each case. Winkler's method (*Zeitsch. anal. Chem.*, 1914, 53, 20) gives good results only in absence of bromide. The presence of bromide in small quantities does not affect the results in the case of those methods in which hydrogen iodide is oxidised to iodine and the latter estimated, for example, Volhard's, Vincent's (A., 1900, ii, 166), and Richard's (*Pharm. Weekblad*, 1903, 40, 157). In the last-mentioned method, it is advisable to let the solution remain for two to three minutes after addition of the tartaric acid. Iodide may be estimated in presence of bromide by adding benzoic acid and potassium iodate, boiling until the iodine has disappeared, then adding potassium iodide and sulphuric acid, and titrating back with thiosulphate.

W. J. W.

**Estimation of Oxygen with Cuprammonium Compounds.**

W. HAEHNEL and M. MUGDAN (*Zeitsch. angew. Chem.*, 1920, **33**, 35).—In the preparation of ammoniacal copper solution for the absorption of oxygen, the usual ammonium carbonate solution employed may, with advantage, be replaced by saturated ammonium chloride solution. The rate of absorption of oxygen is not affected, but the residual gas is free from carbon dioxide derived from the ammoniacal copper solution.

W. P. S.

**The Volumetric Estimation of Sulphates by Oxidation of Benzidine Sulphate with Potassium Permanganate.**

P. L. HIBBARD (*Soil Sci.*, 1919, **8**, 61—65).—A modification of the method of Raiziss and Dubin (compare A., 1914, ii, 671), full details being given. It is shown that both temperature and volume are important factors, which should be kept constant. The solution for the precipitation of benzidine sulphate should be free from organic matter, iron, the heavy metals, nitrates, and phosphates, and should contain between 0.5 and 4.0 mg. of  $\text{SO}_4^{''}$ . It is advisable to use an excess of standard permanganate solution, the oxidation flask being heated in a boiling-water bath for ten minutes. At the end of this time, a slight excess of standard oxalic acid solution is run in, and this is then titrated back with the permanganate solution.

W. G.

**Estimation of the Non-protein Nitrogen in Blood.**

B. ALBERT (*Biochem. Zeitsch.*, 1918, **92**, 397—412).—A modification of the micro-method for estimating the non-protein nitrogen in blood. The blood or serum is freed from its protein by the addition of colloidal iron and 10% potassium sulphate. The filtrate is oxidised with "micro-sulphuric acid," consisting of 15 grams of nitrogen-free potassium sulphate, 5 grams of pure copper sulphate, 100 c.c. of distilled water, and 400 c.c. of pure concentrated sulphuric acid. The distillation is carried out in an apparatus described by the author. The distilled ammonia is received in  $N/200$ -sulphuric acid and estimated iodometrically.

S. S. Z.

**Estimation of Urea Nitrogen in Blood (and Urine).**

B. ALBERT (*Biochem. Zeitsch.*, 1919, **93**, 82—89).—The Lesser-Siebeck micro-method for the estimation of urea nitrogen is considered a very suitable one. Some modifications are recommended.

S. S. Z.

**Estimation of Small Quantities of Arsenic.**

W. VAN RIJN (*Pharm. Weekblad*, 1919, **56**, 1072—1083).—Various methods of estimation of small quantities of arsenic, as in urine, have been investigated. Separation of the arsenic from the material under test is accurately effected by several methods, as follows: (a) Treatment with potassium chlorate and hydrochloric acid (Fresenius and Babo); (b) absorption by ferric hydroxide (Lockemann and Paucke, A., 1911, ii, 720); (c) acidification of the sample with

sulphuric acid, addition of solution of bromine in potassium bromide, then ammonia and magnesia mixture; (d) treatment with ammonia and magnesia mixture, and addition of sodium phosphate (Berntrop). Bloemendaal's apparatus was used for obtaining the mirror; final estimation of this by comparison with a standard mirror was not accurate, and the titration method (Berntrop, A., 1906, ii, 706) was used. Quantities as small as 1 mg. of arsenic per litre were estimated. The estimations were also carried out with wallpapers, paint, and blind materials. W. J. W.

### **Precision Method for the Estimation of Gases in Metals.**

H. M. RYDER (*Trans. Amer. Electrochem. Soc.*, 1918, **33**, 197—204).—The metal to be investigated is mounted as a thin ribbon or filament in an electric light bulb, which is connected to a Toepler pump and exhausted. The temperature of the filament is then raised by an electric current, and the pump set working, so that the gases are continuously removed. The temperature is raised in steps of  $50^{\circ}$  up to the melting point, and the gases evolved at each temperature are measured and analysed. The bulb is water-cooled to prevent the evolution of gases by the glass on heating. Silicon steel was found to give off large volumes of gas at  $730^{\circ}$ . In the analysis, the water vapour and carbon dioxide are frozen out by means of liquid air, and the remaining gases removed. The carbon dioxide is then removed by substituting carbon dioxide snow for the liquid air. The volume of carbon dioxide is measured by reading the pressure existing in the apparatus by means of a MacLeod gauge. It is then pumped out, and the water vapour released into the vessel by removing the refrigerant. The pressure due to this is read by means of a mercury U-tube manometer with optical lever attachment. Oxygen is added to the residual gases, and the hydrogen, methane and carbon monoxide are burnt to carbon dioxide and water, which are estimated as before. Carbon monoxide is added to the residual gases, and serves, after combustion, to estimate the excess of oxygen and any which may have been there originally. Nitrogen is estimated by difference. J. F. S.

### **New Absorption Apparatus for Elementary Analysis.**

FRITZ FRIEDRICHS (*Zeitsch. angew. Chem.*, 1919, **32**, 388).—A compact form of absorption apparatus is described in which the carbon dioxide is absorbed by means of potassium hydroxide solution in a helical tube, which is fixed within the bend of a U-tube. The latter is charged with calcium chloride instead of soda-lime. The use of calcium chloride as a drying agent is preferable to that of sulphuric acid when it is a question of equilibrium being attained. The binary system  $\text{CaCl}_2\text{--H}_2\text{O}$ , in which the phases  $\text{CaCl}_2$ ,  $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$  occur, is univariant, and the tension therefore depends on the temperature, but not on the concentration, whereas the system  $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$ , in which only two phases,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ , are formed, is bivariant, and its tension depends on the concentration as well as on the temperature. The use of both drying

agents, as hitherto, is unsuitable, since the tension of sulphuric acid is lower than that of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ . The gas must therefore be moistened, not dried, in the calcium chloride tube following the sulphuric acid vessel, or the results for hydrogen will be too low; under these conditions, calcium chloride dihydrate must be used instead of anhydrous calcium chloride. It is therefore advisable to discard the sulphuric acid and replace it by 50% potassium hydroxide solution and calcium chloride.

C. A. M.

**Estimation of Combustible Matter in Silicate and Carbonate Rocks.** A. C. FIELDNER, W. A. SELVIG, and G. B. TAYLOR (*U.S. Bureau of Mines*, 1919, Tech. Paper 212).—The method described is a modification of that devised by Lissner (*Chem. Zeit.*, 1910, **34**, 37—38), involving digestion of the silicate material with hydrofluoric and hydrochloric acids, and combustion of the insoluble residue. Carbonate rocks are treated with dilute hydrochloric acid to remove calcium carbonate, etc., and the process is applied to the insoluble residue. [See, further, *J. Soc. Chem. Ind.*, 1920, 155A.]

W. E. F. P.

**The Estimation of Calcium and Magnesium in Different Saline Media.** E. CANALS (*Bull. Soc. chim.*, 1919, [iv], **25**, 655—658. Compare A., 1919, ii, 34, 477).—For the volumetric estimation of small quantities of magnesium it is recommended that the magnesium should first be precipitated as magnesium ammonium phosphate, and then one of two methods adopted.

(1) The precipitate is washed centrifugally with dilute ammonium hydroxide and then dissolved in just sufficient 5% hydrochloric acid, the phosphoric acid in the solution being estimated by titration with an uranium solution (1 c.c. = 0.5 mg.  $\text{P}_2\text{O}_5$ ), using cochineal as an indicator. The results are accurate to 0.2 gram of magnesium.

(2) The precipitate is washed with a saturated aqueous solution of sodium phosphate, and then dissolved in hydrochloric acid, the ammonia present being estimated colorimetrically by means of Nessler's reagent. The results are accurate to 0.01 gram of magnesium.

W. G.

**Spectroscopic Estimation of Small Amounts of Lead in Copper.** C. W. HILL and G. P. LUCKEY (*Trans. Amer. Electrochem. Soc.*, 1917, **32**, 335—343).—A method is described for the rapid estimation of small quantities of lead in copper. A known weight (0.1—1.0 gram) of the sample in the form of a shot is placed in a small cavity in the lower positive graphite electrode of a carbon arc, and a fixed or rotating negative electrode used above. The arc is struck, the light focussed on to the slit of a grating spectroscope, and the time required for the complete disappearance of the bright lead line ( $405.8\mu\mu$ ) from the spectrum, or for its reduction to a definite feeble intensity, is measured by means of a stop-watch. With careful adjustment of the arc, the times vary

regularly with the amount of copper used and with its percentage of lead. Thus 0.2 gram of copper containing 0.004% of lead required 14 secs., whilst 1.0 gram of copper containing 0.038% of lead required 227 secs. A series of experiments made with 0.4 gram samples show that the analyses are sufficiently accurate for use in a copper refinery.

J. F. S.

**Estimation of Mercury.** H. B. GORDON (*Analyst*, 1920, **45**, 41—46).—For the estimation of small quantities of mercury, a coil of copper gauze is suspended in the solution, which has previously received the addition of a small amount of hydrochloric acid and of copper sulphate; the gauze is kept in motion by a motor, and, after a suitable time, is removed from the solution, washed, dried, and weighed. It is then heated in a current of hydrogen, cooled in the same gas, and re-weighed; the loss in weight is due to the volatilisation of the deposited mercury. The volatilised mercury may be collected in a constricted portion of the heating tube and identified by the iodine test. As little as 0.1 mg. of mercury may be detected by the method. Nitrates do not interfere, but antimony, arsenic, bismuth, and silver should not be present, as they are liable to cause error unless the copper gauze is heated at such a temperature that the mercury alone volatilises. [See, further, *J. Soc. Chem. Ind.*, 1920, March.]

W. P. S.

**Detection and Estimation of Very Small Quantities of Chromium in Minerals and Ores containing Silicates and Carbonates.** O. HACKL (*Chem. Zeit.*, 1920, **44**, 63).—One gram of the mineral is fused with eight times its weight of a mixture of sodium carbonate and potassium carbonate, the fused mass is treated with water, a drop of alcohol is added, the mixture heated to reduce and precipitate any manganese compounds present, and the solution is filtered. The filtrate is evaporated, but not so far that alkali salts crystallise out, again filtered, and diluted to a definite volume, which should be from 20 to 50 c.c., according to the quantity of chromium present. The chromium is then estimated colorimetrically, using as a standard a potassium chromate solution containing 0.0511 gram of the salt and a small quantity of sodium carbonate per 200 c.c.; each c.c. of this solution is equivalent to 0.1 mg. of  $\text{Cr}_2\text{O}_3$ .

W. P. S.

**A Very Sensitive Reagent for Cobalt.** I. BELLUCCI (*Gazzetta*, 1919, **49**, ii, 294—298).—One mg. of cobalt in solution may be detected colorimetrically in 1—2 litres of water by means of  $\alpha$ -nitroso- $\beta$ -naphthol, and in about 17 litres of water by means of  $\beta$ -nitroso- $\alpha$ -naphthol (compare Atack, A., 1915, ii, 652; Jones, A., 1918, ii, 410; Bellucci and Chiucini, this vol., ii, 54). One mg. of nickel in 4—5 litres of water may be detected by means of dimethylglyoxime.

T. H. P.

**The Theory of Colour Lakes.** C. BRENNER (*Helv. Chim. Acta*, 1920, **3**, 90—103).—The author has endeavoured to base

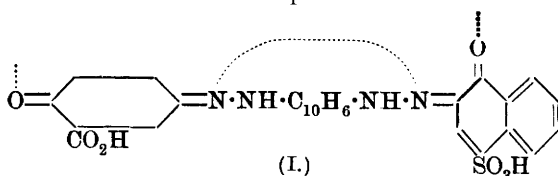
methods for the detection and estimation of minimal amounts of cobalt and copper on the colorations which the metallic ions give with nitrosonaphthols.  $\alpha$ -Nitroso- $\beta$ -naphthol is found to be unsuitable for this purpose in aqueous solution, since the lake is too easily precipitated, whilst chloroform or carbon disulphide solutions (in which cobalt "nitrosite" is readily soluble) are only adapted to the detection, but not to the estimation, of cobalt. On the other hand, the solubility of the lake in water can be sufficiently increased by introducing one or more sulphonic groups into the naphthol molecule. The colour of the lake depends on the number and position of the hydroxy- and sulphonic groups; the yellowest shade is given by the nitroso-derivative of "R"-acid, the deepest red with nitroso-1-naphthol-5-sulphonic acid, and the darkest shade with nitroso-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid (chromotropic acid). In ammoniacal solution, the latter gives a lake when metal and acid are in the proportion of 1 atom to 2 molecules, whilst in sodium hydroxide solution the requisite proportion is 1 : 6; attempts to base a colorimetric process for estimating cobalt on these data were unsuccessful, the results being 10—40% high. On the other hand, the acid can be used for the micro-titration of cobalt, since the yellow, ammoniacal solution of nitrosochromotropic acid yields an immediate intense blue coloration with the cobalt ion, in the formation of which 2 molecules of the acid react with an atom of cobalt; when the cobalt ions have been completely converted into this compound, further addition of the acid causes a change in shade from blue to red. Test analyses show the method to be fairly accurate, but it cannot be used for cobalt in the presence of nickel, although the latter alone may also be estimated by the reagent. The micro-titration of copper can be effected similarly, but a larger excess of the reagent is required to give a definite end-point.

Other substances with properties similar to those of nitrosochromotropic acid are found among azo-dyes which are used with metallic mordants, and among those which in dyeing are subjected to after-chroming. Thus, Diamond Black F gives a deep blue solution in aqueous alkali, which yields differently coloured lakes with ammoniacal solutions of the most various metals; when the metallic ion is completely united with the dye, addition of a further quantity of the latter causes a change in shade towards blue. The possible utility of the method is illustrated at the instance of copper.

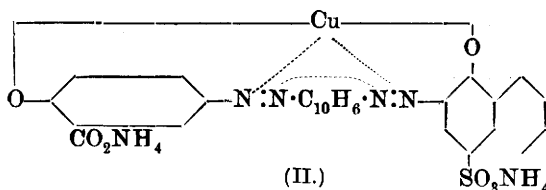
The possibilities of the formation of differently coloured complex compounds have been investigated for twenty different metals and sixteen dyes; such compounds appear to be formed most frequently with magnesium, the alkaline earth metals, and those of the iron group. It is interesting to note that chromium, which is so largely used in mordanting, is allied in this respect with the least reactive metals of the nitrogen family. The capability of the dye to form differently coloured complex compounds which are soluble in ammonia appears to depend on the presence of a hydroxyl group

in the ortho- or para-position to the azo-group, and, as a result of extensive experiments with a number of dyes, it is possible to give methods for the microchemical estimation of copper, silver, magnesium, zinc, cadmium, calcium, strontium, barium, iron, nickel, and cobalt.

The constitution of the lakes and the colour changes involved in the titrations are discussed with particular reference to Diamond



Black. In acid solution, the quinonoid formula (I) is ascribed to the dye in which two strong partial valencies are associated with the oxygen groups, whilst the other partial valencies of the azo-groups satisfy each other. The former valencies are



satisfied by the alkali metal in an alkaline solution, and the dye changes its quinonoid for a benzeneoid structure, whilst, simul-

taneously, the partial valencies of the azo-groups are satisfied by those of the alkali metal. When, however, metallic ions are present in the solution, the subsidiary valencies of which are stronger than those of the alkali metals, the actual lake is produced, as indicated in formula (II).

H. W.

**Estimation of Tungsten in Ferrotungsten.** LUDWIG LÖWY (*Zeitsch. angew. Chem.*, 1919, **32**, 379—380).—Ferrotungsten is completely decomposed when fused with ammonium sulphate and concentrated sulphuric acid, without the porcelain or platinum crucible being attacked, as when the fusion is effected with potassium hydrogen sulphate. The fused mass is dissolved in water, the solution treated with a little nitric acid, and then boiled with dilute (1:5) hydrochloric acid. The precipitated tungstic acid is separated and washed with dilute hydrochloric acid, the filtrate freed from iron by precipitation with ammonia, then acidified, and evaporated to dryness, the residue boiled with dilute hydrochloric acid, and the fresh precipitate of tungstic acid separated. For very accurate analyses, a third precipitation may be made. The united precipitates are ignited until constant in weight, evaporated with hydrofluoric acid, and again ignited and weighed. Any remaining iron may be separated by fusing the residue with sodium carbonate, extracting the mass with water, and weighing the residue of ferric oxide. [See, further, *J. Soc. Chem. Ind.*, 1920, 158A.]

C. A. M.



**Estimation of Uranium and its Separation from Other Rare Elements.** C. A. PIERLÉ (*J. Ind. Eng. Chem.*, 1920, 12, 60—63).—It is shown that good results may be obtained by precipitating uranium with ammonium hydroxide, washing the precipitate with ammonium nitrate solution, and igniting it. Precipitation as uranyl ammonium phosphate by means of ammonium dihydrogen phosphate is also trustworthy, but has the drawback that the ignited uranyl pyrophosphate rapidly absorbs moisture. Precipitation as uranium sulphide and subsequent ignition invariably gives too high results, owing to part of the sulphur being oxidised to sulphate during the ignition. Volumetric estimation of uranium by means of potassium permanganate is inaccurate, owing to over-reduction taking place, and it is not possible to eliminate this or to continue the reduction to a definite point below the uranous condition. A method of separating uranium from vanadium, molybdenum, and tungsten has been based on Peligot's observation (*Ann. Chim. Phys.*, 1842, [iii], 5, 1) that uranyl nitrate is readily soluble in ether. The solution is evaporated to dryness, and the residue of uranyl nitrate, etc., is extracted with ether, in which vanadium pentoxide, molybdenum trioxide, and tungstic trioxide are insoluble. The dry residue should be moistened with nitric acid immediately before the extraction, and shortly after the process has begun, to reconvert into nitrate the partly decomposed uranyl nitrate. Another method of separating uranium from vanadium has been based on the fact that uranyl nitrate is readily soluble, whereas vanadium pentoxide is insoluble in acetic acid of 95% strength or above to which nitric acid has been added in the proportion of 1:20. The solution of uranyl nitrate and sodium metavanadate is evaporated to dryness with nitric acid, and the uranium extracted from the residue by means of the mixed acids. [See, further, *J. Soc. Chem. Ind.*, 1920, 209A.] C. A. M.

**Reaction of Tin Salts.** A. MAZUIR (*Ann. Chim. anal.*, 1919, [ii], 2, 9).—The reaction depends on the insolubility of stannous or stannic iodide in sulphuric acid. Two c.c. of the neutral or slightly alkaline solution containing the tin salt are treated with 2 c.c. of 10% potassium iodide solution and 1 to 2 c.c. of concentrated sulphuric acid. A yellow, crystalline precipitate of tin iodide forms at once if the solution under examination contains not less than 0.1 gram of tin per litre; the precipitate is soluble in chloroform, alcohol, and dilute hydrochloric acid. It is decomposed by ether, iodine being liberated. Arsenic gives a similar reaction, but the arsenic iodide formed is insoluble in dilute or concentrated hydrochloric acid. In the case of antimony, the iodide obtained is flocculent and brick-red in colour. W. P. S.

**Separation and Estimation of Lead and Bismuth.** G. LUFF (*Chem. Zeit.*, 1920, 44, 71).—A nitric acid solution of the two metals is neutralised with ammonia, saturated ammonium nitrite solution and sodium nitrite solution are added, the mixture is

diluted to about 200 c.c., and boiled. When the evolution of nitrogen ceases, the precipitate (bismuth hydroxide or basic bismuth nitrate) is collected on a filter, washed with hot water, then dissolved in nitric acid, the solution evaporated, and the residue ignited and weighed as  $\text{Bi}_2\text{O}_3$ . The filtrate is acidified with acetic acid, and the lead precipitated and weighed as lead chromate. The bismuth oxide, after weighing, should be treated with nitric acid and hydrofluoric acid, again ignited, and washed, to remove traces of silica and alkali respectively.

W. P. S.

### **The Estimation of Acetylene in Gaseous Mixtures.**

J. A. MULLER (*Bull. Soc. chim.*, 1920, [iv], 27, 69—71).—The acetylene is absorbed in ammoniacal cuprous chloride, using a volume of gas containing at the most 10—11 c.c. of acetylene; the solution is acidified with acetic acid, and the cuprous acetylides are collected and washed. The paper and precipitate are transferred to a platinum crucible, and sulphuric acid is added drop by drop until a homogeneous fluid mass is obtained. The excess of acid is gently evaporated, and when fuming has ceased, the crucible is heated to a red heat, cooled, and weighed.

W. G.

**Determination of the Composition of Mixtures of Alcohol and Water by Measurements of Electrical Conductivity.** I. M. KOLTHOFF (*Rec. trav. chim.*, 1920, 39, 126—134).—For the determination of the alcohol content of beer or wine, the following procedure is recommended. The excess of carbon dioxide is removed from the liquid by bubbling air through it, and the liquid is then distilled with magnesium oxide. Fifty c.c. of the distillate are mixed with 10 c.c. of approximately  $N/2$  oxalic acid solution, and the mixture is made up to 100 c.c. with water. The specific conductivities  $x_1$  and  $x_2$  of the mixture and of the original oxalic acid solution diluted to one-tenth with water are then determined. Then  $f_t = 100 \times x_1/x_2$ . This can then be corrected to  $f_{18}$  by means of the temperature-coefficient, and a table is given showing the relationship between  $f_{18}$  and the alcohol content of the distillate.

W. G.

**Specific Reaction of Butylene  $\beta$ -Glycol and of Acetylmethylcarbinol, Products of Butyleneglycollic Fermentation.** LEMOIGNE (*Compt. rend.*, 1920, 170, 131—132).—The characterisation of acetylmethylcarbinol in the products of microbic decomposition of sugars serves to differentiate certain groups of similar microbes, and the following method affords a ready means of detecting traces of this compound. The carbinol is oxidised to diacetyl by means of ferric chloride, the diacetyl being distilled off and detected by precipitation in ammoniacal solution as nickel dimethylglyoxime with a nickel salt and hydroxylamine. By this method it is possible to detect acetylmethylcarbinol at a dilution of 1 in 1,000,000. The reaction is not given by any other of the products of fermentation.

W. G.

**Microchemical Method of Estimating Dextrose. II.**

IVAR BANG (*Biochem. Zeitsch.*, 1918, **92**, 344—347. Compare A., 1918, ii, 279).—It is found that the potassium iodate employed by the author in his modified method for the micro-estimation of sugar in blood does not keep well. He therefore uses free iodic acid instead. The solution is prepared by dissolving 0.3567 gram of pure potassium iodate in 10 c.c. of 20% sulphuric acid. 2.5 Grams of copper sulphate ( $\text{CuSO}_4 + 5\text{H}_2\text{O}$ ) may also be added to it at the same time, and the solution is made up to 1 litre.

The author finds that by means of Willstätter and Schüchl's method, 0.1—0.5 mg. of sugar can be estimated. However, this method cannot be employed in the estimation of sugar in blood. Blood containing 0.107% of sugar showed a content of 0.22% and 0.23% by this method. S. S. Z.

**Adsorption Compounds and Adsorption. V. The Adsorption Compounds of Cuprous Oxide.** L. BERCZELLER (*Biochem. Zeitsch.*, 1919, **93**, 230—237).—In precipitating cupric hydroxide from cupric salts with sodium hydroxide, some of the alkali is adsorbed by the cupric hydroxide. The black hydroxides adsorb more of it than the blue ones. Iodate ions are also adsorbed by cupric hydroxide, but in this case the blue hydroxides adsorb more of it than the black. The presence of sugar prevents the adsorption of sodium hydroxide by cupric hydroxide. S. S. Z.

**Estimation of Small Quantities of Sugar in the Presence of the Higher or Lower Products of Protein Degradation.**

ERWIN LAST (*Biochem. Zeitsch.*, 1919, **93**, 66—82).—The higher products of protein degradation, such as albumoses and peptones, the presence of which interferes with the estimation of sugar, can be removed by means of mercuric chloride in neutral solution. The sugar can then be estimated by Bertrand's method. In the presence of acids, the precipitation of these products is incomplete. An excess of mercuric chloride must also be avoided in order to ensure good results. Two grams of mercuric chloride per gram of peptone are found to be a suitable quantity. The presence of monoaminoacids does not affect the accuracy of the sugar estimation by Bertrand's method; ereptone, however, does influence the results. This is due to the special atomic grouping in ereptone, which, on boiling with alkali hydroxide, liberates ammonia, and this dissolves some of the cuprous oxide. Ereptone can be removed from sugar solutions also by precipitation with mercuric chloride in neutral solution. The removal of both the higher and lower products of protein degradation with mercuric nitrate according to the Patein-Dufau method conduces to accurate results. S. S. Z.

**Estimation of Lactose in Altered Milks.** E. HELDT (*Bull. Soc. chim.*, 1919, [iv], **25**, 617—621).—A more detailed account of work already published (compare A., 1919, ii, 84).

W. G.

**Modification of the Phenylhydrazine Method of Estimating Pentosans.** PAUL MENAUL and C. T. DOWELL (*J. Ind. Eng. Chem.*, 1919, **11**, 1024—1025).—The material is distilled with sulphuric acid instead of hydrochloric acid, and the furfuraldehyde is estimated in the distillate by precipitating with a known excess of phenylhydrazine, filtering off the hydrazone, and determining the excess of phenylhydrazine in the filtrate. For this purpose, an aliquot part of the filtrate is heated with ammoniacal copper sulphate solution, and the nitrogen evolved is measured, the reaction previously employed by Ebler for the determination of hydrazine (A., 1906, ii, 53) being quantitative also in the case of phenylhydrazine. [See, further, *J. Soc. Chem. Ind.*, 1920, 170A.]

J. H. L.

**A Microchemical Method for the Estimation of Acetone.** M. RICHTER-QUITTNER (*Biochem. Zeitsch.*, 1919, **93**, 163—172).—A microchemical method in which 1—2 c.c. of urine and 1·5—3 c.c. of alkali need only be used. The urine is distilled once with steam in the presence of acetic acid, and a second time with dilute sulphuric acid. Blood or plasma need only be distilled once, and instead of the steam, air is passed through the heated flask. The titration of the distilled acetone is carried out with *N*/100-iodine and *N*/100-sodium thiosulphate. 0·1 Mg. of acetone in 100 c.c. can be estimated with accuracy by this method. The quantity of urine and blood used must contain not less than 0·04 mg. of acetone.

S. S. Z.

**Microchemical Reactions of Veronal, Luminal, and Propional.** L. VAN ITALLIE and A. L. W. E. VAN DER VEEN (*Pharm. Weekblad*, 1919, **56**, 1112—1117; *J. Pharm. Chim.*, 1919, [vii], **20**, 337—343).—Small traces of the derivatives of barbituric acid separated from urine by treatment with lead acetate and hydrogen sulphide may be converted into an easily identifiable, crystalline form by sublimation. Veronal may be separated as monoclinic crystals from its solution in sodium hydroxide by the addition of an acid, potassium dichromate, or ammonium phosphate. Lead acetate gives an amorphous mass, which becomes crystalline on boiling. Ammoniacal silver nitrate gives an irregular, crystalline mass of large, simple crystals of veronal-silver. With thallium nitrate, crystals of veronal-thallium are formed. Luminal and propional have only to be separated in the uncombined state. A crystal of ammonium phosphate introduced into a drop of a solution of these in sodium hydroxide causes the separation of the free acids in the form of drops which only gradually change into crystals, probably rhombic.

W. J. W.

**Estimation of "Saccharin" in Urine.** GEORGE S. JAMIESON (*J. Biol. Chem.*, 1920, **41**, 3—8).—Urine is treated with lead acetate and filtered. After acidifying with hydrochloric acid, the "saccharin" is extracted by ether, the ether removed by evapor-

ation, and the "saccharin" extracted from the residue by ether. The ether is removed, and the resulting residue is fused with sodium carbonate. From an estimation of sulphur in the fused product, the amount of "saccharin" may be deduced. J. C. D.

### **The Estimation of Aniline in Commercial Anilines.**

WILLIAM JAMES SANDERSON and WILLIAM JACOB JONES (*J. Soc. Chem. Ind.*, 1920, **39**, 8T).—A method of estimation is given which is based on a determination of the freezing point of the sample. The purity is deduced by reference to a table, which is provided, showing the freezing points of dry mixtures of aniline with varying proportions (1–7% by weight of the mixture) of each of benzene, phenylhydroxylamine, nitrosobenzene, *p*-aminophenol, nitrobenzene, *o*- or *p*-toluidine, *m*-phenylenediamine, and xylidine. J. K.

**Formaldehyde Titration of Amino-acids in Aqueous Solutions or in Urine.** W. MESTREZAT (*Bull. Soc. Chim. Biol.*, 1919, **1**, 107–113).—The methods employed by Ronchèse (cited by Maillard, *Compt. rend. Soc. Biol.*, 1911, **61**, 653) are insufficiently accurate. J. C. D.

**Urea and Hypobromite.** L. LESCŒUR (*J. Pharm. Chim.*, 1919, **20**, 305–314, 343–351, 374–381).—The volume of nitrogen liberated by the action of alkaline hypobromite solution on urea is always less than that required by theory; too low results are also found if the urea is calculated from the amount of carbon dioxide formed or of the hypobromite used in the reaction. The deficit is to some extent dependent on the proportion of free alkali present, and decreases, but never quite disappears, as the quantity of free alkali is increased; it appears to be due to the conversion of a part of the urea into sodium cyanate. W. P. S.

**Ureometer.** P. SEYOT (*Ann. Chim. anal.*, 1920, [ii], **2**, 11–13).—The apparatus consists of a graduated tube open at its lower end, whilst the upper end, above the zero point, is bent over and downwards for a short distance, where it is blown out to form a bulb. A short side-tube with a tap is provided at the top of the bend. The bulb has a tubulure at the side into which is ground the neck of a small cylindrical bulb. The latter contains the hypobromite solution, whilst the urine or other liquid under examination is placed in the larger bulb. The whole apparatus is placed in a cylinder of water, the level of the latter then adjusted to the zero point by manipulating the tap, and the smaller bulb then turned (by means of the ground-in joint) so that the hypobromite solution mixes with the urine in the larger bulb. The evolved nitrogen displaces water from the graduated tube, and the volume of the nitrogen is noted after the water-level has been adjusted. If 1.3 c.c. of urine is taken for the estimation, each c.c. of nitrogen is equivalent to 1 gram of urea per litre of urine. W. P. S.

**Identification of Traces of Hydrocyanic Acid.** L. CHELLE (*Bull. Soc. Pharm., Bordeaux*, 1919; from *Ann. Chim. anal.*, 1920, [ii], 2, 21—24. Compare A., 1919, ii, 529).—The following tests may be used for the identification of traces of hydrocyanic acid: *Phthalein test*.—A red coloration is obtained when a cyanide solution is treated with a drop of alkaline phenolphthalein solution reduced previously with zinc, and a drop of 0.1% copper sulphate is added. *isoPurpurate test*.—If a cyanide solution is heated with the addition of alkaline picric acid solution, an orange coloration develops after a few hours. *Ammoniacal silver iodide test*.—The reagent is prepared by diluting a mixture of 10 c.c. of *N*/1000-silver nitrate solution, 2 c.c. of ammonia, and five drops of 19% potassium iodide solution to 100 c.c.; this reagent gives a turbidity with a cyanide solution. For instance, if a turbidity is obtained when 1 c.c. of the cyanide solution is treated with 0.2 c.c. of the reagent, less than 0.001 mg. of hydrocyanic acid is present; with 0.005 mg. of hydrocyanic acid, 1 c.c. of the reagent is required. *Ferrocyanide test*.—This is the most characteristic reaction of hydrocyanic acid; it may be used for the identification of hydrocyanic acid in silver cyanide and mercuric cyanide. W. P. S.

**Sensitiveness of some Cyanide Reactions.** JOHN B. EKELEY and ICIE C. MACY (*Proc. Colorado Sci. Soc.*, 1919, 11, 269—274).—Working directly with solutions of potassium cyanide, the Prussian blue test gives positive results (a blue precipitate on keeping) at a dilution of  $1:7 \times 10^4$  (at about  $1:17 \times 10^4$  for hydrogen cyanide). One hundred c.c. of potassium cyanide solution ( $1:7 \times 10^5$ ) give a definite result after acidifying with 10 c.c. of 1% tartaric acid and distilling off about 2 c.c.; this corresponds with a dilution of hydrogen cyanide about  $1:1.7 \times 10^6$ . The hanging-drop method with silver nitrate gives positive results with solutions of potassium cyanide ( $1:8 \times 10^6$ , corresponding with hydrogen cyanide at a dilution of about  $1:19 \times 10^6$ ) when 100 c.c. are exposed to the drop of silver nitrate for fifteen minutes. The Schönbein test gives positive results with potassium cyanide solutions at a dilution of  $1:18 \times 10^6$  in the light and  $1:23 \times 10^6$  in the dark (equivalent to  $1:43 \times 10^6$  and  $1:55 \times 10^6$ , respectively, for hydrogen cyanide). This test should be performed in closed vessels in the dark to secure trustworthy results, and only at extreme dilutions does it indicate the presence of hydrogen cyanide and exclude the presence of other substances (chlorine, bromine, hydrogen peroxide, hydrogen chloride) which are known to respond at high concentrations. CHEMICAL ABSTRACTS.

**Estimation and Separation of Pyridine and Ammonia.** E. B. R. PRIDEAUX (*Trans. Faraday Soc.*, 1919, 15, 137—147).—Precise information as to the conditions for the titration of pyridine and of ammonia in the presence of pyridine, and of the separation of the two by distillation, has been obtained by application of the electrochemical theory. Congo-red is the correct

indicator for pyridine, and nitric acid the best acid. A correct indicator for the titration of ammonia in the presence of pyridine is  $\alpha$ -naphtholphthalein. Both ammonia and pyridine are estimated with sufficient accuracy provided that pyridine is not present in excess. Rosolic acid may be used if the bases are titrated directly, and the pyridine is present in amount considerably less than the ammonia. Ammonia and pyridine may be partly separated by distillation from a solution of which the acidity is maintained at about  $p_H=3$  to 4 (reddish-brown to Congo, orange to methyl-orange). The first part of the distillate contains most of the pyridine, the second most of the ammonia, so that the titrations just described may be used.

J. R. P.

**Estimation of Indole in Biological Media.** HARPER F. ZOLLER (*J. Biol. Chem.*, 1920, **41**, 25—36).—The usual preliminary steam distillation of the indole solution is abandoned and replaced by direct distillation, care being taken to have the solution adjusted to a hydrogen-ion concentration of  $p_H$  9.2 (see this vol., i, 250). The distillation is continued until all but about 10 c.c. have been driven over, the distillate being collected in a 100 c.c. volumetric flask and made up to the mark. A portion of the distillate containing not more than 0.20 mg. of indole is measured into a test-tube of convenient size, and two drops of 1.0% solution of sodium nitrite and five drops of concentrated sulphuric acid are added. The tube is shaken and left for five minutes for the nitroso-reaction to approach equilibrium. The contents are then extracted with three portions of 3 c.c. of *isobutyl* or *isoamyl* alcohol, each portion being drawn off with a pipette and placed in a test-tube having a 10 c.c. graduation. *isoButyl* or *isoamyl* alcohol is then added to bring the contents of the tube up to 10 c.c., and the colour is matched against a series of standards prepared by similar treatment of solutions containing a known amount of pure indole.

The method is stated to be simple, trustworthy, and rapid. The relative sensitivities of Herter's naphthaquinone reaction and the nitroso-reaction were found to be 1:2,000,000 and 1:1,500,000 respectively.

A warning is sounded against the use of the vanillin test proposed by Steensma (*A.*, 1906, ii, 315).

The rate at which the equilibrium of the nitroso-indole reaction is reached depends on the factors of concentration and temperature. At temperatures from 30—90°, the full depth of colour is obtained in a few seconds, but higher temperatures tend to destroy the coloured compound when in aqueous solutions. In pure *isobutyl* alcohol the colour is not destroyed by heating for several hours at 100°. In actual analyses, the test should not be carried out at temperatures above 30°.

J. C. D.

**Detection of other Cinchona Alkaloids in Salts of Quinine.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 451—459).—Kerner and Weller's method has many disadvantages, and only gives

accurate results under certain conditions. The following method is suitable for quinine sulphate, but is inapplicable to other salts. 0.5 Gram of quinine sulphate is boiled gently for one minute with 250 mg. of sodium sulphate and 10 c.c. of water. Water is then added to restore the original volume, and the mixture cooled to 15°, with shaking. The liquid, with the precipitate, is kept below 18° for twenty-four hours, and then filtered through glass wool. Three drops of 4*N*-sodium hydroxide are added to the filtrate, which is then heated on the water-bath for half an hour. After twelve hours, the solution is examined for the presence of a precipitate. The test is sensitive to 1% of cinchonidine. In regard to the nitroprusside test, the author does not confirm Kruss's opinion of its sensitiveness, and failed to devise a means of increasing this. De Vrij's chromate test is considered to be a suitable substitute for Kerner and Weller's method. For quinine bisulphate, 0.5 gram is boiled with 20 c.c. 2*N*-sodium acetate until the liquid is clear. Then 3 c.c. of 10% potassium chromate are added, and further treatment is carried out by de Vrij's method. For quinine, 0.5 gram is taken, together with 3 c.c. of *N*-sulphuric acid and 20 c.c. of 2*N*-sodium acetate, and the test continued as above. Quinine hydrochloride may be tested exactly as described by de Vrij.

W. J. W.

**Estimation of Albumin in Urine.** OTTO MAYER (*Zeitsch. anal. Chem.*, 1919, **58**, 337—346).—A reagent described previously by the author (*A.*, 1914, ii, 80) for the estimation of albumin in urine is altered in composition in order to render it more sensitive. Ten grams of mercuric chloride, 65 grams of sodium chloride, and 25 grams of citric acid are dissolved in 500 c.c. of hot water and the solution is filtered after a few days. This solution will give a ring reaction in about ten minutes with as little as 0.0002% of albumin, whilst 0.001% of albumin is denoted by the appearance of a turbid zone within three minutes. If the urine contains more than 0.001% of albumin, the test is repeated after dilution until the reaction is just observable, and the quantity of albumin present then calculated from the degree of dilution.

W. P. S.

**Estimation of Catalase in Blood.** MEYER BODANSKY (*J. Biol. Chem.*, 1919, **40**, 127—130).—In making estimations of catalase by the method employed by Burge (*Amer. J. Physiol.*, 1916, **41**, 153), it was found that different samples of hydrogen peroxide often gave results which differed by 15—35%. It was experimentally shown that the reaction of the medium is one important factor in determining the activity of catalase. Consequently, caution must be exercised in maintaining uniform conditions when a series of determinations are being made.

J. C. D.

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## General and Physical Chemistry.

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**The Optics of Disperse Systems. IV.** I. LIFSCHITZ and GEORG BECK (*Kolloid Zeitsch.*, 1920, **26**, 58—66. Compare A., 1918, ii, 181, 253; this vol., ii, 137).—The chemical processes occurring during change in the colloidal state and their effect on the change in the light absorption is theoretically considered. An attempt is made to use the published work on the refractometric measurements of colloids to explain the rôle of the change in the colloidal state in the change in light absorption. The density, refractive index, molecular and specific refractivities for the *C*, *D*, and *F* lines have been measured for solutions of twenty organic acids and their sodium salts in methyl alcohol at 25°. It is shown that the increase in refraction from acid to sodium salt is different in the different cases, but with acids which form salts accompanied by a rearrangement or by exercising subsidiary valencies there is an extraordinarily large change. The increase in refraction in salt formation is independent of simultaneous peptisation or colloid formation, and an abnormally large increase in the refraction cannot be explained by a change in the dispersity. It is also shown that a very large percentage of cases of vario-chromism and polychromism are to be explained by intramolecular action of subsidiary valencies, and that chromoisomerism is to be similarly explained. J. F. S.

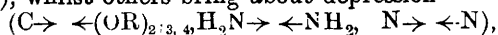
**Influence of Position and Accumulation of Substituents on Spectrochemical Behaviour. V. Alkyloxyacetic Acids.** A. KARVONEN (*Acad. Sci. Fennicae*, 1916, [A], **10**, No. 8, 1—7; from *Chem. Zentr.*, 1919, iii, 987. Compare this vol., ii, 129).—The alkyloxyacetic acids exhibit optical values slightly lower than that of acetic acid itself. H. W.

**Influence of Position and Accumulation of Substituents on Spectrochemical Behaviour. VI. Esters of Keto-alcohols, COMe·[CH<sub>2</sub>]<sub>n</sub>·O·CO·Me.** A. KARVONEN (*Acad. Sci. Fennicae*, 1916, [A], **10**, No. 8, 1—7; from *Chem. Zentr.*, 1919, iii, 987).—Further investigation with fresh materials shows that the optical values increase somewhat with increase in the relative distance between the carbonyl group and that of oxygen connected to two carbon atoms in the cases of esters of the lower alkyloxy-aliphatic acids and keto-alcohols. H. W.

**Influence of Position and Accumulation of Substituents on Spectrochemical Behaviour. VII. Ether-Alcohols, RO·[CH<sub>2</sub>]<sub>n</sub>·OH.** A. KARVONEN (*Acad. Sci. Fennicae*, 1916, [A], **10**, No. 9, 1—8; from *Chem. Zentr.*, 1919, iii, 981).—Spectrochemical investigation of the monomethyl, ethyl, and propyl ethers

of ethylene glycol and of the monomethyl and ethyl ethers of trimethylene glycol shows these compounds to be closely related optically. H. W.

**Influence of Position and Accumulation of Substituents on Spectrochemical Behaviour. VIII. Mutual Spectrochemical Action of Hydroxyl Groups.** A. KARVONEN (*Acad. Sci. Fennicae*, 1916, [A], 10, No. 10, 1—10; from *Chem. Zentr.*, 1919, iii, 981).—Investigation of ethylene and trimethylene glycols showed that two hydroxyl groups in direct union with one another cause marked exaltation, which is progressively diminished by the successive introduction of methylene groups between the hydroxyls. Certain atoms or atomic groups directly united with one another cause optical exaltation ( $\text{HO} \leftrightarrow \text{OH}$ ,  $\text{O} \leftrightarrow \text{O}$ ,  $-\text{S} \leftrightarrow -\text{S}-$ ,  $-\text{Se} \leftrightarrow -\text{Se}-$ ), whilst others bring about depression



a third section being neutral or nearly so ( $\text{H}_2\text{N} \rightleftharpoons \text{OH}$ ). This action cannot readily be ascribed to supplementary valencies, and not invariably to the existence of double bonds between the atoms. H. W.

**Effect of an Electric Field on the [Spectrum] Lines of Argon and Oxygen.** E. BÖTTCHER and F. TUCZEK (*Ann. Physik*, 1920, [iv], 61, 107—112).—The effect of an electric field of 26,000 *V/cm* on the spectrum lines of argon, and on both the spark and arc lines of oxygen, has been investigated. In the case of argon, the lines are absolutely unaffected by the field; the same result was obtained with the spark lines of oxygen. Of the arc lines the 3—7 members of the I subsidiary triplet series showed a displacement towards the red which increased with increasing member number. The four lines  $\lambda\lambda$  4846, 4743, 4634, and 4559 are observed in the spectrum under the influence of the field, and have not before been observed. They are displaced toward the violet. The intensity increases with increasing wave-length, and the series ceases with the most intensive member without any indication of a further less intensive member. The *p*-components are considerably more intensive than the *s*-components. With increasing strength of field the intensity of the lines with longer wave-lengths increases more rapidly than that of those with shorter wave-lengths. The lines are regarded as belonging to a sharp subsidiary series of the I triplet subsidiary series. J. F. S.

**Spectro-analytical Investigation of the Luminosity of Decomposing Ozone.** KARL STUCHTEY (*Zeitsch. wiss. Photochem.*, 1920, 19, 161—197).—The spectrum of the luminosity of an oxygen-nitrogen mixture in an ozoniser has been photographed and shown to be made up of the second positive group of the nitrogen spectrum, the emission spectrum of the Y-oxide of nitrogen (Warburg and Leithäuser, A., 1906, ii, 743; 1907, ii, 342; 1909, ii, 226, 227), and the visible emission spectrum of ozone. The emission spectra agree absolutely with the well-known absorption

spectra. On heating ozone at  $400^{\circ}$  in a specially constructed oven a strong luminosity is observed. The light shows both the visible and the ultra-violet spectra of ozone. A mixture of nitrogen and ozonised oxygen heated in the same furnace shows, in addition to the emission spectrum of ozone, also the emission spectrum of the  $Y$ -oxide of nitrogen. An explanation of the mechanism of the luminosity is given, and it is shown that the luminosity does not depend on presence of oxidisable substances. J. F. S.

**A Helium Series in the Extreme Ultra-violet.** THEODORE LYMAN (*Nature*, 1919, 104, 314; *Science*, 1919, 50, 481—483).—By using a powerful disruptive discharge in helium a fairly strong line, in addition to those previously reported for the helium spectrum, was found to appear at wave-length 1640.2, and a fainter line at about 1215.1. Experimental evidence is thus afforded for the existence of the lines 1640.1 and 1214.9 as calculated from theoretical considerations. CHEMICAL ABSTRACTS.

**Some New Spark Spectra in the Extreme Ultra-violet.** LÉON BLOCH and EUGÈNE BLOCH (*Compt. rend.*, 1920, 170, 320—322).—Using the spectrograph with a fluorspar prism, previously described (*ibid.*, 226), the authors have studied the spectra from a condensed spark between metallic electrodes in hydrogen in the case of four metals. Cadmium gave a spark spectrum extending to  $\lambda=1500$ , and the rays have been measured down to  $\lambda=1600$ . Bismuth gave a spectrum to  $\lambda=1500$ , the rays being measured to  $\lambda=1550$ . The spark spectrum of nickel is very rich in rays in the extreme ultra-violet, these being measured to  $\lambda=1540$ . Down to  $\lambda=1650$  there is a great similarity between the arc and spark spectra. For silver the rays were measured down to  $\lambda=1496$ . Nickel gave a doublet,  $\lambda=1550.7$  and  $1548.2$ , and silver gave a doublet,  $\lambda=1551.3$  and  $1548.7$ . W. G.

**Line Spectra of Cadmium and Zinc in the Electrodeless Ring Discharge.** A. HAGENBACH and H. SCHUMACHER (*Zeitsch. wiss. Photochem.*, 1919, 19, 129—142).—The spectra of zinc and cadmium produced from an electrodeless discharge have been measured and compared with the arc and spark spectra of these elements. It is shown that the spectrum coincides neither with the arc spectrum nor with the line spectrum in either case, but contains lines of both spark and arc spectra as well as a number of new lines. The intensity of the various lines is also very different from that of the lines in the arc and spark spectra. In the case of cadmium, lines are measured from  $\lambda 6467.4$  to  $2183.1$ , and forty-four new lines lying between  $\lambda 5511.0$  and  $2436.25$  are recorded both in the international system and in Rowland's system. In the case of zinc, the lines measured lie between  $\lambda 6362.58$  and  $2252.87$  and thirteen new lines lying between  $\lambda 3186.24$  and  $2246.88$  are recorded. It is also shown that under suitable conditions a band spectrum can also be obtained. J. F. S.

**Band Spectrum of Zinc from the Electrodeless Ring Discharge.** A. HAGENBACH and H. SCHUMACHER (*Zeitsch. wiss. Photochem.*, 1919, **19**, 142—148. Compare preceding abstract).—The band spectrum of zinc obtained from an electrodeless discharge has been measured over the range  $\lambda$  4894.9—3469.5, and compared with existing measurements. A large number of new bands are recorded. J. F. S.

**Measurement of the Arc Spectrum of Iron below  $\lambda$  2373 according to the International System.** H. SCHUMACHER (*Zeitsch. wiss. Photochem.*, 1919, **19**, 149—158).—The iron spectrum of smaller wave-length than  $\lambda$  2373 has been photographed and measured. The wave-lengths are given on the international system, and an accuracy of about 0.03 Å. is claimed for the values. As source of light an iron arc burning with 4 amperes and 220 volts was used. The values are compared with those of Kayser and Runge. J. F. S.

**Theory of Absorption Spectra.** I. LIFSCHITZ (*Schweiz. Chem. Zeit.*, 1918, **2**, 58; from *Chem. Zentr.*, 1919, iii, 970).—A reply to Kauffmann's criticisms (*A.*, 1917, i, 391) of the author's views (*A.*, 1917, ii, 435). H. W.

**The Chromophore Function. V. Optical Properties of some Heavy Metal Complexes.** I. LIFSCHITZ and ERNST ROSENBOHM (*Zeitsch. wiss. Photochem.*, 1920, **19**, 198—214. Compare *A.*, 1917, ii, 62, 435).—The absorption spectra of the heavy metal complexes consist in general of at least three bands which lie between  $\lambda$  6000 and  $\lambda$  2000 Å. units. Of these, that with the longest wave-length depends mainly on the nature of the central atom; the next band depends on the nature of the co-ordinated groups if the central atom is the same. The band with shortest wave-length is not so completely investigated, because in many cases it lies so far in the ultra-violet as to be unmeasurable with the apparatus employed. All the work on the subject tends to show that this band is displaced more toward the longer wave-lengths in the presence of bivalent co-ordinated groups than in the presence of univalent groups. J. F. S.

**Calculation of the Frequency Limits of Absorption  $K$  and  $L$  of the Heavy Elements.** LOUIS DE BROGLIE (*Compt. rend.*, 1920, **170**, 585—587).—For tungsten, platinum, gold, lead, bismuth, thorium, and uranium examined, Vegard's formula gives results for the frequency limits of absorption,  $K$  and  $L$ , which are much more nearly in agreement with the mean of the observed results than those calculated by Bohr's formula. W. G.

**Absorption Coefficients of Solutions for Monochromatic Radiation.** E. O. HULBURT and J. F. HUTCHINSON (*Carnegie Inst. Pub.*, 1918, **260**, 6—69).—The absorption-coefficient of solutions of inorganic salts in water and in different alcohols has been

measured at intervals of  $20\ \mu\mu$  to  $40\ \mu\mu$  throughout the spectrum region from  $600\ \mu\mu$  to  $1300\ \mu\mu$ . For each salt a series of solutions varying in concentration from saturation to moderate dilution was prepared, and the absorption curve drawn for each solution. The molecular absorption-coefficient,  $A$ , of the salt was calculated for each wave-length and plotted against  $c$ , the concentration of the salt in gram-molecules. Solutions of cobalt chloride in water, ethyl, propyl, *isobutyl*, and *isoamyl* alcohols were examined by the photographic method; the values of  $A$  changed with the concentration, and the absorption curves for the higher alcohols were similar to those for ethyl alcohol. The following solutions were also examined: cobalt nitrate and sulphate, nickel chloride (anhydrous and the hexahydrate), nitrate and sulphate in methyl, ethyl, and propyl alcohols; ammonium ferric alum in water; chromic chloride, nitrate, and sulphate; and potassium permanganate. The relation between  $A$  and  $c$  has been determined from the data thus obtained. In general,  $A$  is not constant. Sometimes it decreases with dilution, in other cases increases with dilution, and also passes through a minimum; a maximum was not obtained. The deviations of  $A$  from a constant value were usually small, except at certain points in the spectrum, which in general were situated at the edges of absorption bands.

No theory adequately explains the observations.

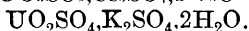
CHEMICAL ABSTRACTS.

**Colour Antagonism or Chemical and Electrical Polarity of the Spectrum.** GABRIELE RABEL (*Zeitsch. wiss. Photochem.*, 1919, 19, 69—128).—The long-wave half of the spectrum from the yellowish-green to the infra-red is termed positive light, whilst the short-wave half from bluish-green to ultra-violet is termed negative light. It is shown that phosphorescent light is produced by negative light and extinguished by positive light. Phosphorescent substances and certain classes of organic substances change their colour when subjected to negative light, but in positive light regain the original colour. Silver salts are reduced by negative light, but are oxidised by positive light. Certain biological and chemical reactions occur in the reverse direction in negative light from that in positive light. Electrodes which are sensitive to light undergo opposite potential changes in negative light from those in positive light. The retina of the eye belongs to the light sensitive electrodes. The movements of lower organisms are influenced in opposite ways by positive and negative light. In high-tension discharge in hydrogen, in the red hydrogen layers, the maximum potential lies in the luminous layer, the minimum in the dark space between the layers, whilst with the blue hydrogen layers the maximum is in the dark space and the minimum in the luminous layer. In the bluish-red double layers the dark space shows neither maximum nor minimum but is positive to the blue layer and negative to the red layer. If a plate covered with sodium chloride is brought into a luminous layer discharge, reduction (that is, formation of a blue

coloration) occurs in the luminous layer in the blue discharge, and in the dark space in the red discharge. J. F. S.

### Fluorescence and Absorption of the Uranyl Sulphates.

E. L. NICHOLS and H. L. HOWES (*Physical Rev.*, 1919, [2], **14**, 293—305).—The fluorescence spectrum of the uranyl sulphates consists of eight equidistant bands, the first and eighth of which disappear at the temperature of liquid air. The remaining bands are resolved into groups of narrow line-like bands, the homologous members of which form series having constant frequency intervals, ranging from 85.7 in  $\text{UO}_2\text{SO}_4 \cdot \text{Cs}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  to 83.0 in



The fluorescence groups are distinguished by a strong pair of bands about eight frequency units apart and several weak bands, some of which are doublets. There is a shift of all bands towards the violet, with increasing molecular weights, of about fifteen frequency units in passing from the spectrum of uranyl sulphate to that of the caesium double salt. The absorption spectra of the sulphates are made up of series of bands having a frequency interval of 70.3 on an average. These absorption series extend into group 7 of the fluorescence without break of interval. There are many reversals where fluorescence and absorption overlap. The reversing region is, therefore, one group further towards the red than in most spectra of the uranyl compounds. CHEMICAL ABSTRACTS.

### Fluorescence and Absorption of the Uranyl Acetates.

E. L. NICHOLS, H. L. HOWES, and FRANCES G. WICK (*Physical Rev.*, 1919, [2], **14**, 201—221).—The paper deals with the fluorescence and absorption spectra of the two known forms of uranyl acetate and of thirteen double uranyl acetates as they appear when excited at the temperature of liquid air. The essential identity of the spectra of the double acetates of lithium, potassium, calcium, manganese, and strontium, both as regards the location of the principal bands and the structure of the fluorescence groups, is established and the deviations from this type occurring in the spectra of the uranyl acetates containing barium, ammonium, rubidium, sodium, magnesium, zinc, silver, and lead are considered. The approximate identity of frequency intervals for all series and for all salts is likewise established, the interval being 84.76.

CHEMICAL ABSTRACTS.

### Quanten Theory Basis of Photochemistry. E. WARBURG

(*Zeitsch. Elektrochem.*, 1920, **26**, 54—59).—A theoretical paper in which it is shown that every photochemical reaction is characterised by the specific photochemical action  $\phi$ , that is, by the number of gram cal. of heat absorbed per mol. The fundamental law of photochemical reaction is, that energy of frequency  $\nu$  is absorbed in quanta by the reacting molecules. The molecules which absorb the light radiation are termed "photochemical reserved molecules," and from the law stated, the number of these may be calculated. Valency radiation is the radiation which in the reserving

of 1 mol. of the photolyte is absorbed by it. The indicated photochemical equivalent ( $p$ ) is the number of mols. which are reserved in the absorption of 1 gram-cal. The effective photochemical equivalent is the number of mols. which are decomposed or changed by the absorption of 1 gram-cal. It is equal to the specific photochemical action  $\phi$  when this is calculated on the number of decomposed or changed molecules.  $\phi/p$  is the efficiency relationship. Einstein's photochemical equivalent law says that every absorbing or reserved molecule is by the act of absorption decomposed or changed, and when the secondary processes are known it determines the efficiency relationship for which values  $\geq 1$  are obtained. The law is rigidly held in isolated cases only, because in general the reserved molecules, or at least a part of them, do not undergo primary change for the following reasons: (1) the valency radiation is smaller than the molecular decomposition energy; (2) energy is lost during the absorption of the radiation; and (3) the chemical change only takes place as a secondary process as in the case of photolytic isomerisation.

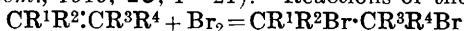
J. F. S.

### Photochemical Studies. VIII. Periodic Light Reactions.

JOH. PLOTNIKOW (*Zeitsch. wiss. Photochem.*, 1919, 19, 22—39).—The action of chlorine on  $\alpha$ -cyanocinnamic acid in carbon tetrachloride solution under the influence of light of wavelength  $\lambda=436\mu$  has been investigated at  $17^\circ$ . It is shown that there is no formation of a chlorine additive compound, and that the nitrile concentration has no influence on the reaction, but chlorine is used up linearly with time, and its use is due to a hitherto unknown reaction between carbon tetrachloride and chlorine. The reaction between carbon tetrachloride and chlorine was therefore investigated. It is shown that the absorption of chlorine is linear both with blue light  $\lambda=436\mu$  and ultraviolet light  $\lambda=366\mu$ . Using the whole of the light from a uviol lamp, a periodic change in the concentration of the chlorine is observed. Further experiments show that in light, pure carbon tetrachloride yields free chlorine. The reaction is discussed, and the possibility of periodic light reactions shown. Two types of such reactions are indicated: (1) Periodic light reactions are a necessary consequence of the stationary condition of photochemical processes, and must occur periodically so long as light of various wavelengths acts. (2) Periodic light reactions are the result of the combination of different opposing reactions, which are brought into existence by light of different wave-lengths, and are influenced by different catalysts, and consequently tend to an equilibrium condition.

J. F. S.

**Photochemical Studies. VII. Equilibria in Photochemical Addition of Bromine.** JOH. PLOTNIKOW (*Zeitsch. wiss. Photochem.*, 1919, 19, 1—21).—Reactions of the type



are reversible, and are of such a nature that the equilibrium position, in the dark as well as in the light, depends on the temperature,

concentration, nature of the solvent, intensity of light, and the nature of the radicles  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$ . The reaction between bromine and  $\alpha$ -cyanocinnamic acid in light has been investigated:  $\text{CHPh}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{H} + \text{Br}_2 \rightleftharpoons \text{CHPhBr}\cdot\text{CBr}(\text{CN})\cdot\text{CO}_2\text{H}$ . The reactions were carried out in carbon tetrachloride solution, using light of wave-length  $\lambda = 436 \mu$  at  $7^\circ$ . It is shown that bromine does not react as  $\text{Br}_2$ , but as  $2\text{Br}$ , and the reaction taking place is proportional to the square of the absorbed light energy. The displacement of the equilibrium is proportional to the light intensity. The equilibrium formula for the reaction has the form

$$Q = J(1 - e^{-ip(b-y)^2(a-y)})/py,$$

where  $y$  is the equilibrium constant of the dibromide,  $p$  the thickness of the layer of solution,  $a$  the initial concentration of the nitrile,  $b$  the initial concentration of the bromine,  $i$  the normal light absorption constant of bromine (for  $\lambda = 436 \mu$  it is  $0.2156$  per millimol. concentration), and  $J$  the light intensity. The temperature-coefficient of the dark reaction of the dibromide decomposition is determined from the corresponding equilibrium displacement and found to be  $2.14$ . It is suggested that the extreme ultra-violet rays have the opposite action to the long waves on this reaction.

J. F. S.

**Spectral Photoelectric Sensitivity of Silver Sulphide and several other Substances.** W. W. COBLENTZ and H. KOHLER (*Bull. Bur. Standards*, 1919, 15, 231—249; *Sci. Paper*, 1919, No. 344).—Data are given of the change in the electrical resistance of the sulphides of silver and bismuth when exposed to radiations from  $0.6 \mu$  in the visible spectrum to  $3 \mu$  in the infra-red. Galena, cylindrite, pyrites, and jamesonite did not show photoelectric sensitivity for the highest spectral radiation intensities available. The sulphides of silver and bismuth are sensitive from  $0.6 \mu$  to  $1.8 \mu$ . The photoelectric response for silver sulphide becomes fatigued at the ordinary temperature. The change in resistance of the crystal when exposed to radiation is first negative and then positive, the resultant change being negative and approximately one-fifth of the original change. At  $-158^\circ$  this polarisation phenomenon disappears, and the response to radiation is the same as that of other substances, such as selenium or molybdenite. The sensitivity is greatly increased when the temperature is lowered to  $-158^\circ$ . The sensitivity curve is quite symmetrical, and shows a maximum at  $1.2 \mu$ . An increase in the intensity of the exciting radiation shifts the maximum towards the long wave-lengths.

A spectral photoelectric sensitivity curve of bismuthinite was obtained at  $-166^\circ$ , maxima occurring at  $0.64 \mu$  and  $1.08 \mu$ .

CHEMICAL ABSTRACTS.

**Photo-oxidation of Organic Compounds by Chromates.** JOH. PLOTNIKOW (*Zeitsch. wiss. Photochem.*, 1919, 19, 40—56).—The photo-oxidation of ethyl alcohol of various concentrations by ammonium chromate and ammonium dichromate in light of wave-



length  $\lambda = 436 \mu\mu$  has been studied at  $20^\circ$ . It is shown that the velocity constant may be calculated by means of a linear equation, and that it is proportional to the concentration of the alcohol. Increase in the salt concentration causes the reaction velocity to approach a maximum. The absorption constants of the salt solutions have been measured, and are found to be a function of the alcohol concentration and show a maximum. The dichromate follows Beer's Law, but the chromate does not. The absorption changes brought about by the alcohol do not affect the reaction velocity. The velocities of oxidation are the same with chromate as with dichromate. The temperature-coefficient of the reactions is 1.02. These reactions in general exhibit a perfectly normal photochemical behaviour.

J. F. S.

**Biochemical Action of Light.** F. SCHANZ (*Pflüger's Archiv*, 1918, **170**, 646—676; from *Physiol. Abstr.*, 1918, **3**, 552).—Observations on the lens of the eye have shown that the effect of light is to render protein less soluble. Some authors have attributed this change to certain substances accompanying the protein. The presence of acetone in diabetes coupled with the frequent occurrence of lenticular opacity suggested a series of experiments in which equal amounts of a protein solution in a series of quartz tubes were treated with increasing amounts of acetone. Series 1 and 2 were placed in the sunshine, whilst series 3 was incubated in the dark at  $38^\circ$ . After four days the contents of the various tubes were equalised by appropriate additions of acetone, the only distinction being that in series 1 and 3 the added acetone had been previously treated with light, whereas in series 2 it had not. The amount of precipitation, after the addition of ammonium sulphate, sodium chloride, and acetic acid by the method previously described, was then noted in each case. The results showed that the change from a more to less soluble condition of the protein was due to the effect of light on the protein itself; the reaction was, however, increased by the presence of acetone. The amount of acetone breakdown (amount of gas formed) was tested after exposure to a quartz lamp of acetone (1) in ordinary glass (absence of shorter rays than  $\lambda 30 \mu\mu$ ); (2) in quartz (absence of shorter rays than  $\lambda 200 \mu\mu$ ); and (3) shaded with a "euphos" glass screen (rays shorter than  $\lambda 400 \mu\mu$ ). The results showed that acetone absorbed and was acted on by the ultra-violet rays alone. The author maintains that chemically pure organic salts are quickly broken down by the action of light in the absence of iron. Some quartz spectrographs figured in the text show absorption of the violet rays by protein and other substances, the greatest absorption being exhibited by acetaldehyde and acetone. Certain coloured substances, such as eosin, hæmatoporphyrin, and chlorophyll, act as optical sensitisers; eosin is non-toxic unless the organism is exposed to intense light. Mice die suddenly if exposed to daylight after previous injection of hæmatoporphyrin, and various lesions of the skin occur in sub-acute cases. It is suggested that the brilliant

colourings of flowers, etc., is to enable the organism to select the particular light rays required. Other experiments show that the growth of plants is affected by ultra-violet rays. J. C. D.

**The Reaction of Proteins to Light.** F. SCHANZ (*Pflüger's Archiv*, 1917, 169, 82—86; from *Physiol. Abstr.*, 1917, 2, 584).—The author refers to his previous work on the lens proteins, and also to Neuberg's work. Proteins are more sensitive to light than Neuberg considers, and experiments are given which show that quartz lamp rays can effect in them changes in solubility, etc., so that albumins then show the characters of globulins. J. C. D.

**Some Observations on the Action of Coal on a Photographic Plate.** ERIC SINKINSON (*T.*, 1920, 117, 165—170).

**Chemical Actions of Radiation.** EUGÈNE WOURTZEL (*Le Radium*, 1919, 11, 289—298, 332—347. Compare A., 1914, ii, 18, 238).—The chemical action of  $\alpha$ -rays from radium emanation on hydrogen sulphide, ammonia, nitrous oxide, and carbon dioxide has been investigated. When the reaction is not accompanied by secondary reactions, it is found that the amount of decomposition, under the same conditions of volume, pressure, and temperature, is proportional to the amount of emanation present. This is the case with the reactions  $\text{H}_2\text{S} = \text{H}_2 + \text{S}$  and  $\text{NH}_3 = \text{N} + 3\text{H}$ . The effect increases with the dimensions of the vessel, and the volume, but tends to a maximum value, corresponding with the total utilisation of the energy of the radiation. If  $K$ ,  $K_\infty$  are the velocity constants for particular conditions and for total utilisation of energy respectively,  $R$  is the radius of the vessel, and  $p$  the pressure, then, when  $K > 0.5K_\infty$ , it is found that  $K = K_\infty (1 - C/Rp)$ , where  $C$  is a constant. When  $K < 0.5K_\infty$ , the relation is represented by a line tangent to the above curve, and passing through the origin. The decomposition of nitrous oxide is complicated by a secondary reaction, namely, the formation of nitric peroxide from the nitric oxide and oxygen set free in the initial reactions  $\text{N}_2\text{O} = \text{N}_2 + \text{O}$ ;  $\text{N}_2\text{O} = \text{NO} + \text{N}$ . Contrary to the statement of Ramsay and Cameron, carbon dioxide is only very slowly decomposed by  $\alpha$ -rays. No theoretical conclusions are drawn from the results beyond the statement that the decompositions do not follow Faraday's law. A full account of the apparatus used is given. J. R. P.

**New Arrangement for the Röntgen [Ray] Crystallographic Investigation of Crystalline Powders.** HELGE BOHLIN (*Ann. Physik*, 1920, [iv], 61, 421—439).—A new arrangement is described, in which by means of a cylindrical arc-shaped scattering surface, made of a compressed, crystalline powder, interference lines can be produced. One edge of the lines is sharp and may be geometrically defined, whereby an increased accuracy over that of the previously described methods is rendered possible. It is shown that the sharpness and the position of the line edge is in-

dependent of the width of the slit and of the depth to which the radiation penetrates. By means of photographs of the interference lines the space grating of thorium, nickel, and magnesium has been determined by this method. It is shown that thorium and nickel have face-centred cubic lattices, whilst magnesium has a lattice made up of two simple interpenetrating hexagonal lattices. J. F. S.

**An Experimental Determination of the Critical Electron Velocities for the Production of the Ionisation and Radiation on Collision with Argon Atoms.** FRANK HORTON and ANN CATHERINE DAVIES (*Proc. Roy. Soc.*, 1920, [A], **97**, 1—23. Compare A., 1919, ii, 210).—In the conclusion of Franck and Hertz that ionisation occurred in argon when the velocity of the colliding electrons was raised to 12 volts, the ionisation of the gas could not be distinguished from photoelectric effects of radiation produced by the collisions. By methods similar to those previously employed for helium, it has been shown that, when electrons bombard argon atoms, a radiation is produced when the electrons attain a velocity corresponding with 11·5 volts, which is not accompanied by ionisation of the argon, but at 15·1 volts ionisation of the argon takes place. The latter potential corresponds, according to the quantum relation, with a wave-length of 817 Å.U., which is in accord with the spectroscopic investigation of the extreme ultra-violet spectrum of argon by Lyman, which he found terminated abruptly at 800° Å.U. Evidence has been obtained that at 15·1 volts not all the collisions are fruitful in producing ionisation, and that the fraction of fruitful collisions is increased greatly by intense 11·5 volt radiation. The minimum ionisation velocity, 15·1 volts, however, is the same whether the argon is exposed to weak or intense 11·5 volt radiation. F. S.

**Investigation of the Effects of Electron Collisions with Platinum and with Hydrogen, to ascertain whether the Production of Ionisation from Platinum is due to Occluded Hydrogen.** FRANK HORTON and ANN CATHERINE DAVIES (*Proc. Roy. Soc.*, 1920, [A], **97**, 23—43).—During the investigation of electron collisions with helium it was found that positive ions were produced from a positively charged platinum gauze bombarded with electrons of minimum velocity corresponding with 11 volts, and this has been more fully investigated to determine whether it is due to the metal or to attached hydrogen. This voltage is subject to a correction for the velocity at which the electrons leave the tungsten filament, and the mean of all the corrected results gives 13·0 volts as the critical electron velocity for the production of the ionisation, which does not agree with the usually accepted value of the "ionisation potential" of hydrogen (11 volts). In the same apparatus the production of ionisation in hydrogen was investigated, hydrogen being introduced through a palladium tube heated in a flame, and the conclusion was reached that the first critical velocity (13 volts) is not due to hydrogen at all, but probably

to the platinum itself. In hydrogen it was found that a radiation is produced at an electron velocity of 10·5 volts, a second type of radiation at 13·9 volts, an ionisation at 14·4 volts, and a second type of ionisation at 16·9 volts. These four velocities correspond probably with radiation from the hydrogen atom and molecule and ionisation of the hydrogen atom and molecule respectively, the values calculated from Bohr's theory being 10·2 instead of 10·5 for the first, 13·6 instead of 14·4 for the third, and 16·3 instead of 16·9 for the fourth. It is desirable that these critical velocities be further examined in an apparatus specially designed for the purpose.

F. S.

**Melting Point<sup>3</sup> of Lead Isotopes.** M. E. LEMBERT (*Zeitsch. Elektrochem.*, 1920, **26**, 59—60).—The melting points of pure lead chloride and lead chloride containing Ra-G chloride have been determined and shown to agree to within 0·06%, that is, to within 0·5°. The material used for the determination was that used by Richards and Lemberg for atomic-weight determinations, and from which the values 207·15 and 206·57 respectively were obtained (A., 1914, ii, 683). The present results confirm the assumption of Fajans (A., 1915, ii, 206) that  $v^2m$  is constant for isotopes as against the view of Lindemann (*Nature*, 1915, **95**, 7) that  $v$  is constant.

J. F. S.

**The Radioactivity of Bavarian Rocks and Waters and of the Fluorspar of Wölsenberg.** F. HENRICH (*Zeitsch. angew. Chem.*, 1920, **33**, 5—8, 13—14, 20—22).—An investigation of the distribution of radioactivity in the springs, rocks, and minerals of Bavaria, including also French Switzerland, the Fichtelgebirge, and the Oberpfalz, is described with details of the activity of a large number of springs expressed in Mache units (*M.U.*). The springs in the chalk mountains of French Switzerland were but feebly active, but in the granitic areas of the Fichtelgebirge most of the springs had an activity between 10 and 100 *M.U.* and four were over 100 *M.U.* The minerals tobernite and autunite occurred in these districts in the granite. A special examination of the gases from one of the springs showed the unusual composition of about 12% of oxygen and the rest "unabsorbable."

A description is given of the fluorspar of Wölsenberg ("Stinkfluss"), in which the dark blue and violet-coloured varieties emit a peculiar odour on being crushed, which is undoubtedly due to the evolution of free fluorine. The origin of this is considered to be due to the action of rays of radioactive substances, dissociating the calcium fluoride, with coloration of the mineral due to colloidal calcium and evolution of free fluorine. By acting on fluorspar with radium rays the colour is easily produced, but not the odour of fluorine.

F. S.

**Dependence of the Dielectric Constants of Water, Ethyl Alcohol, Methyl Alcohol, and Acetone on Pressure.** G. FAJENBERG (*Ann. Physik*, 1920, [iv], **61**, 145—166).—The dielec-

tric constant of water, ethyl alcohol, methyl alcohol, and acetone has been determined at temperatures (16.3—20°) over the pressure range 7—200 atms. The mean change in the dielectric constant per atmosphere increase in pressure is found to be 0.0046% for water, 0.0097% for ethyl alcohol, 0.0102% for methyl alcohol, and 0.016% for acetone. The refraction constants  $(n-1)/d$ ,  $(n^2-1)/d$ , and  $(n^2-1)/(n^2+2) \cdot 1/d$  are calculated for the above-named liquids at the pressures named. In the case of water and both alcohols a good agreement is found for the expression  $(n^2-1)/d$ , both at low and high pressures. In the case of acetone, owing to insufficient knowledge of the compressibility, conclusions are not arrived at. Using the results of Ortqvist (A., 1911, ii, 961), the values of  $(n^2-1)/d$  and  $(n-1)/d$  are calculated for benzene and ethyl alcohol. In the case of benzene the value of  $(n^2-1)/d$  is constant over the range 1—500 atmospheres: but with ethyl alcohol all three values show considerable irregularity over the same pressure range. The very large values of the Wiener number  $u$  for water and the two alcohols confirm the suggestion of Röntgen that the ratio of polymerised to non-polymerised molecules changes with increase of pressure. J. F. S.

**[Electrical] Conductivity of Solid Salts and Mixtures of Salts.** ROBERT KETZER (*Zeitsch. Elektrochem.*, 1920, 26, 77—84).

—The specific conductivity of pastilles of lead chloride, lead bromide, and mixtures of these substances with varying amounts of sodium and potassium chloride and bromide respectively has been determined at 37°. Electrical contacts were made with amalgamated copper plates, and it is shown that differences in conductivity amounting to 12% may be occasioned by variations in the pressure employed in making the pastille. It is shown that the large increase in conductivity found by Fritsch (A., 1897, ii, 301) on mixing the haloids of lead and mercury with alkali haloids, does not occur if moisture is completely removed and if the mixture is not heated to a high temperature. It is shown that the previous treatment of lead chloride has a marked influence on the conductivity. In the case of the mixtures, it is found that heating before pressing increases the conductivity to a considerable extent. Thus 2% of sodium chloride in lead chloride increases the conductivity of the lead chloride 109—170 times, if the previous heating was carried out in moist air, in a vacuum, or in chlorine; on heating in dry air the increase was 41 times. The very smallest additions to lead chloride produced a considerable increase in conductivity; thus, 0.001% of sodium chloride increased the conductivity 45 times if the mixture was melted in chlorine before pressing. No proportionality was found between the concentration of the alkali chloride and the increase in conductivity. J. F. S.

**Form of the Conductivity Function in Dilute Solutions.**

CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1920, 42, 1—18).—A theoretical paper, in which the method adopted by Washburn (A., 1918, ii, 55) for calculation of the value of  $k_0$  is examined

The author is not able to agree either with Washburn's conclusions or with his interpretation as to the limiting character of the law of mass action. J. F. S.

**Conductivity and Viscosity of Organic and Inorganic Salts in Formamide and in Mixtures of Formamide with Ethyl Alcohol.** P. B. DAVIS and H. I. JOHNSON (*Carnegie Inst. Pub.*, 1918, **260**, 71—96).—The conductivity and the viscosity in formamide solution of (a) metallic nitrates and formates (common anion), and (b) sodium salts of organic acids (common cation) have been measured, and also the behaviour of certain representative salts in mixtures of formamide and ethyl alcohol has been studied. The molecular conductivities of ammonium, potassium, sodium, calcium, strontium, and barium nitrates in formamide, which has a greater dissociating power than water, are much smaller than in aqueous solution. Evidence of complex solvent formation is obtained with the calcium, strontium, and barium salts in formamide and in water. From the conductivities and viscosities of the formates of rubidium, ammonium, lithium, sodium, barium, and strontium in formamide at 15°, 25°, and 35°, the conclusions are drawn that these salts, like the nitrates, are more strongly dissociated at low dilutions in formamide than in water, that the temperature-coefficients of the conductivities are of the same order of magnitude for the alkali formates, but are greater for the alkaline-earth formates, and that rubidium and ammonium formates increase the viscosity less than sodium and lithium formates.

From conductivity and viscosity measurements in formamide at 15°, 25°, and 35° of sodium *m*-bromo-, *m*-amino-, and 3:5-dinitrobenzoate, benzoate, salicylate, benzenesulphonate, and succinate, the conclusions are drawn that (a) the conducting capacity of the first three salts is approximately the same, and the same is true of the next three. All monobasic salts have nearly the same conductance, which is about half that of the dibasic salt; (b) no relation exists between the conductivity and the constitution of the organic salts, and the same is true of the viscosity.

Data were also obtained on the molecular conductivity and the viscosity of tetramethylammonium iodide, rubidium iodide, lithium nitrate, and calcium nitrate in mixtures of formamide and ethyl alcohol. The first three salts show an increase in molecular conductivity up to a concentration of 25% formamide and 75% ethyl alcohol, where a maximum is reached, a fact explicable by an increase of ionic mobility at this point. Cæsium, rubidium, and potassium salts lower the viscosity of water, but increase that of formamide.

CHEMICAL ABSTRACTS.

**Electrical Conductivity of the Sodium Salts of certain Organic Acids in Absolute Alcohol at 15°, 25°, and 35°.** H. H. LLOYD and A. M. PARDEE (*Carnegie Inst. Pub.*, 1918, **260**, 99—118).—An extension of previous work on the electrical conductivity and dissociation of various organic acids in alcoholic solu-

tion, involving a study of the sodium salts of the organic acids in absolute alcoholic solution to obtain first the  $\lambda_n$  values for these salts and then the  $\lambda_n$  values for the acids. Absolute alcoholic solutions of thirty-two sodium salts were prepared, and the conductivities at 15°, 25°, and 35° over the range  $N/50$  to  $N/20,000$  were determined. Goldschmidt's previous results were confirmed. The  $\lambda_n$  values were obtained by extrapolation, using the function  $1/\lambda = 1/\lambda_n + K(C\lambda)^{n-1}$  developed by Naves and Johnston. The Kohlrausch formula did not give satisfactory results. The  $\lambda_n$  values at 25° were obtained for all the salts, and by combination with the  $\lambda_n$  values for hydrogen and sodium chlorides the limiting conductivity at 25° of thirty-one organic acids in absolute alcoholic solution was calculated. The dissociation and affinity constants of these acids in such solution can be calculated from the  $\lambda_n$  values. There is a great similarity in the conductivity of these organic acids in alcohol. Little can be said of the relation between chemical composition and conductivity. No difference was found between aliphatic and aromatic derivatives, and the position of substituents in the latter appeared to be without influence on the conductivity.

CHEMICAL ABSTRACTS.

**The Positive Influence which the  $\alpha$ -Diols Exercise on the Conductivity of Boric Acid.** J. BÖESEKEN (*Rec. trav. chim.*, 1920, **39**, 178—182).—[With W. ROST VAN TONNINGEN.]—Diethylmalonic acid has  $K_a = 2.8 \times 10^{-3}$ , and is notably much stronger than diglycollic acid (compare A., 1916, ii, 595). It might be expected, therefore, to have a feebler negative influence on the conductivity of boric acid, but the diminution found is almost the same in the two cases.

[With W. F. TH. HENDRIKSZ.]—Measurements with  $\beta$ -nitro- $\beta$ -methylpropane- $\alpha$ -diol give results almost equal to those of glycerol and much less than those of pentaerythritol. W. G.

**The cycloHexane-1:2-diols and the Flexibility of the Benzene Ring.** J. BÖESEKEN and J. VAN GIFFEN (*Rec. trav. chim.*, 1920, **39**, 183—186).—Measurements have been made with the *cis*- and *trans*-cyclohexane-1:2-diols to determine their influence on the conductivity of boric acid. The influence of both isomerides is manifestly negative, but the influence of the *cis*-isomeride is slightly more feeble than that of the *trans*-isomeride. The *cis*-diol shows a greater tendency to form complexes than the *trans*-diol. The authors explain the difference of behaviour of these two isomerides on the hypothesis that the flexibility of the cyclohexane ring permits of the hydroxyl groups of the *cis*-form obeying more easily their natural repulsion.

W. G.

**Increase in the Conductivity of the  $\alpha$ -Keto-acids by Boric Acid, as a Consequence of the Formation of  $\alpha$ -Hydroxy-acids by Hydration:  $R \cdot C(OH)_2 \cdot CO_2H$ .** J. BÖESEKEN and W. ROST VAN TONNINGEN (*Rec. trav. chim.*, 1920, **39**, 187—190).—Trimethylpyruvic acid, like pyruvic acid itself (compare A., 1916,

ii, 209), exerts a marked positive influence on the conductivity of boric acid itself. thus confirming the view previously expressed (*loc. cit.*) that the  $\alpha$ -keto-acids in aqueous solutions are hydrated and behave like dihydroxy-compounds. Trimethylpyruvic acid is notably much weaker than pyruvic acid, and the dehydration takes place more easily, so that it apparently exerts a negative influence even at moderate dilutions. W. G.

**Overpotential and Catalytic Activity.** ERIC K. RIDEAL (*J. Amer. Chem. Soc.*, 1920, **42**, 94—105).—The influence of temperature on overpotential has been determined at a series of temperatures for platinum, copper, and zinc. In the case of zinc, there is no relationship between the calculated and observed temperature-coefficient, the latter only amounting to 0.31 millivolt per degree at 37°. In the case of copper and platinum, a higher coefficient is observed, the values being 2.2 millivolts per degree and 0.17 millivolt per degree respectively. These values are three to four times as large as the calculated values. It is suggested that overpotential is a measure of the energy required for the desorption of hydrogen from a metal surface. Metals with low latent heats of desorption are catalytically active, the activity increasing with decreasing overpotentials. Metals with overpotentials exceeding 0.455 volt are catalytically inert, and no metal can possess an overvoltage exceeding 1.80 volts. The calculated values of the catalytic activities of the metals are in agreement with Sabatier's qualitative observations. A suggestion is made for the mechanism of the process of desorption on the radiation hypothesis. J. F. S.

**Resemblances between the Properties of Surface Films in Passive Metals and in Living Protoplasm. II.** RALPH S. LILLIE (*Science*, 1919, **50**, 416—421. Compare A., 1919, i, 606).—Most ions activate passive iron at varying rates and the stability of the surface film in any solution, and hence the preservation of the passive state, is dependent on the oxidising properties of the dissolved substance. Continued oxidation seems to be necessary for preservation of passivity. Ions of strong oxidising properties tend to stabilise regardless of charge, for example, the dichromate, permanganate, silver, gold, and platinum ions. The haloid ions have a strong activating influence, the rate being proportional to the concentration. Salts with terminal oxygen in union activate only very slowly. The cation has not so large an effect, but passivity is retained longer in solutions of heavy metal salts. Any condition that confers increased stability on the surface film prevents or retards its destruction in an activating solution. Hence oxidising anions or cations more noble than the experimental metal antagonise the activating effects of other ions. The antagonism between sodium and calcium so characteristic in biological systems is not exhibited by passive iron. Anæsthetics, except ethyl nitrate, show no retarding effect towards activation as they do in protoplasm, but



this is not to be expected since solution in the organic solvents of the protoplasm, particularly lipoids, is not paralleled by any process of solution in the metals.

CHEMICAL ABSTRACTS.

**Simple Hydrogen Electrode.** C. H. BAILEY (*J. Amer. Chem. Soc.*, 1920, **42**, 45—48).—The vessel and electrode for preparing a simple hydrogen cell may be constructed as follows. A piece of 7 mm. bore tube is blown out at one end to form a bulb 15 mm. diam.; the tube is then bent to form an angle of about  $45^\circ$  at a distance of 50 mm. from the top of the bulb. The other limb of the tube is about 80 mm. long, and is fitted with a ground-glass stopper. The metal electrode is a thin gold disk 5 mm. diam. welded to a piece of thin platinum wire and fused into the side of the shorter limb of the tube about 5 mm. above the bend. The gold foil is platinised in the usual way. The tube is filled with the liquid under investigation, and then by means of a fine tube the bulb is filled with pure hydrogen, thus expelling some of the liquid. It is then stoppered, care being taken to exclude all air, and vigorously shaken until the solution is saturated with hydrogen. Connexion is made with the standard electrode by removing the stopper and placing the syphon tube well down the longer limb. The electrode is stated to give trustworthy results, and to be very rapid in its action.

J. F. S.

**A Gas Collecting Tube.** ERICH MÜLLER (*Zeitsch. Elektrochem.*, 1920, **26**, 76—77).—A gas burette for collecting the gases evolved at electrodes during electrolysis is described. The novelty of the apparatus lies in the tap which is attached at the bottom of the burette; this is a heavy tap with a key bored in T-shape, so that the horizontal bore will give access to the burette and the vertical bore to a side-tube to which the levelling tube is attached.

J. F. S.

**New Cadmium Vapour Arc Lamp.** FREDERICK BATES (*Phil. Mag.*, 1920, [vi], **39**, 353—358).—A small quartz cadmium vapour lamp is described. The lamp is in the form of an inverted U-tube of 10 c.c. capacity, and is fitted with two long quartz capillaries at its ends, by means of which the tungsten wire electrodes are admitted. The electrodes are fastened into the capillaries by means of lead seals. The lamp is filled by distilling, from a quartz bulb attached at the bend of the U-tube, a gallium-cadmium alloy containing 2—3% of gallium. The presence of the gallium renders the cadmium soft, and so prevents breakage of the lamp when the metal solidifies. The distillation is carried out at 0.001 mm. pressure, and when sufficient has been distilled into the lamp the narrow tube by which the bulb is connected is sealed. The lamp will burn with 110 volts and 3 amperes with a drop of 14 volts across the terminals, but is more efficient with a current of 7 amperes and a drop of 25 volts. To start the lamp one limb must be heated with a bunsen flame. The spectrum of the light thus produced is prac-

tically that of pure cadmium; the lamp is durable, and requires little attention, and furnishes an intense monochromatic source of red light by means of the line  $\lambda 6439 \text{ \AA}$ . J. F. S.

**Magnetic Susceptibilities of Hydrogen and some other Gases.** TAKÉ SONÉ (*Phil. Mag.*, 1920, [vi]. **39**, 305—350, and *Sci. Rep. Tohoku. Imp. Univ.*, 1919, **8**, 115—167).—The magnetic susceptibility of air, oxygen, carbon dioxide, atmospheric nitrogen, chemically pure nitrogen, argon, and hydrogen has been determined with reference to water  $= -0.720 \times 10^{-6}$ . The following specific susceptibilities ( $\chi \cdot 10^6$ ) at  $20^\circ$ , and volume susceptibilities ( $\kappa \cdot 10^6$ ) at  $0^\circ$  and 760 mm. are found: air,  $\chi = 23.85$ ,  $\kappa = 0.03084$ ; oxygen,  $\chi = 104.1$ ,  $\kappa = 0.1488$ ; carbon dioxide,  $\chi = -0.423$ ,  $\kappa = -0.000836$ ; chemically pure nitrogen,  $\chi = -0.265$ ,  $\kappa = -0.000331$ ; atmospheric nitrogen,  $\chi = -0.360$ ,  $\kappa = -0.000452$ ; argon,  $\chi = -5.86$ ,  $\kappa = 0.0104$ ; hydrogen,  $\chi = -1.982$ ,  $\kappa = -0.0001781$ . The susceptibility of air as determined is very close to that calculated from the values for the constituent gases, which indicates that the additive rule holds for the susceptibility of gases. The susceptibility of nitrogen is found to be diamagnetic, a fact which is opposed to the values of all other observers except Pascal, who found it had a value about 50% greater than the present value. The specific susceptibilities of gaseous and solid carbon dioxide have the same value. The present results are considered in the light of Bohr's atomic model for hydrogen. J. F. S.

**Moment of Inertia of the Magneton.** R. GANS (*Ann. Physik.*, 1920, [iv]. **61**, 396—397).—A theoretical paper, in which the moment of inertia of the magneton of a number of elements is calculated. This value is of the same order in most cases, and lies between  $0.761 \times 10^{-43}$  and  $60.2 \times 10^{-43}$ . The moment of inertia of platinum is  $67.7 \times 10^{-40}$  and of anhydrous manganous sulphate  $12.4 \times 10^{-40}$ . J. F. S.

**Magneto-chemistry of the Chromic Chlorides.** JOSÉ BALTA ELIAS (*Anal. Fis. Quim.*, 1918, **16**, 467—483).—The magnetic susceptibility of aqueous solutions of the green and the violet chromic chloride was determined at different degrees of concentration, temperature and acidity, and during transformation of either modification into the other. Quincke's method was employed for dilute, and the solenoid method for concentrated, solutions. The susceptibility of the solutions of either salt was found to be independent of the concentration, hence they comply with Wiedemann's law (that is the susceptibility is an additive property, obtained as the sum of those of its components). The conversion of the green into the violet solution and vice versa was not marked by any change in the magnetic constant within the intervals in which the measurements were made (up to eight hundred and eighty-six hours). Hence the two modifications have the same magnetic constant, whereas their

other physical properties are different. It is inferred that—unlike cobalt, the magnetic properties of which undergo profound changes in certain co-ordination compounds—the linking between chromium and the other atoms or radicles in its co-ordination sphere is effected through the more external electronic orbits of the atom. The existence of nineteen magnetons in the chromium atom is confirmed (compare Cabrera and Marquina, A., 1917, ii. 355). The magnetic constant of both salts decreases in dilute solutions, but in presence of hydrochloric acid hydrolysis is repressed and the (stable) green chloride regenerated. The figures obtained for the molecular susceptibilities ( $\chi^{(M)}$ ) of the two compounds are given below, together with those obtained by Feytis (A., 1913, ii, 381):

	Elias.	Feytis.
$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ .....	$6181.10^{-6}$	$5920.10^{-6}$
$[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ ...	$6179.10^{-6}$	$6100.10^{-6}$

W. R. S.

### Establishing of the Absolute Temperature Scale.

FREDERICK G. KEYES (*J. Amer. Chem. Soc.*, 1920, **42**, 54—59).—A theoretical paper, in which the work of Buckingham and of Chappuis on the absolute temperature scale is considered from the point of view of the author's new equation of state, which is based on the Bohr conception of the atom (*Proc. Nat. Acad. Sci.*, 1917, **3**, 323). J. F. S.

### Characteristics of the Gouy Thermo-regulator. T. S.

SLIGH, jun. (*J. Amer. Chem. Soc.*, 1920, **42**, 60—68).—The paper describes a modification of the usual type of electrical thermo-regulator in which the fixed contact element is replaced by an oscillating contact element, and shows that such a regulator will reduce the periodic variations of the bath temperature and the erratic variations due to variations of the mercury surface to a fraction of the values obtainable with the usual form of thermo-regulator. A periodic variation in bath temperature of less than  $0.0001^\circ$ , as indicated by a temperature indicator, having a natural period of about five seconds is easily obtained. By the use of an oscillating contact regulator, variations of mean bath temperature due to variations in external conditions are reduced below the values usually obtained. Characteristic equations are derived for both the fixed and oscillating type of thermo-regulator, and these equations, together with experimental data, have been used to draw a comparison between the two types of regulator. J. F. S.

**Variation of Thermal Conductivity during the Fusion of Metals.** SEIBEI KONNO (*Sci. Rep. Tohoku. Imp. Univ.*, 1919, **8**, 169—179).—The thermal conductivity has been determined for tin ( $18$ — $498^\circ$ ), lead ( $18$ — $601^\circ$ ), bismuth ( $18$ — $584^\circ$ ), zinc ( $18$ — $578^\circ$ ), aluminium ( $18$ — $800^\circ$ ), and antimony ( $0$ — $692^\circ$ ). The thermal conductivity of tin, lead, zinc, and aluminium decreases with rise of temperature up to the melting point. On melting the thermal

conductivity of these metals decreases abruptly and to a considerable extent. The thermal conductivity of bismuth and antimony decreases to a minimum, which lies at  $160^{\circ}$  and  $182^{\circ}$  respectively, and then slowly rises to the melting point. On melting the thermal conductivity of bismuth increases considerably, whilst that of antimony appears to decrease slightly. The thermal conductivity of the molten metals in all cases decreases slightly with increase in temperature. The changes in thermal conductivity run parallel with the changes in electrical conductivity with rise in temperature.

J. F. S.

**Variation of Atomic Heats as a Function of the Temperature.** MATHEUS D'A. ALBUQUERQUE (Pamphlet [Portuguese], 1919, 1—19).—A theoretical discussion.

**Melting Points of Pure Metals.** W. GUERTLER and M. PIRANI (*Zeitsch. Metallkunde*, 11, 1—7; from *Chem. Zentr.*, 1919, iii, 910—911).—The following are given as the most trustworthy figures for the melting points of the elements: Ag,  $961^{\circ}$ ; Al,  $658^{\circ}$ ; As,  $850^{\circ}$  (?); Au,  $1063^{\circ}$ ; B,  $2400^{\circ}$ ; Ba,  $850^{\circ}$ ; Gl,  $1300^{\circ}$  (?); Bi,  $270^{\circ}$ ; C,  $>3600^{\circ}$ ; Ca,  $809^{\circ}$ ; Cd,  $321^{\circ}$ ; Ce,  $700^{\circ}$ ; Cl,  $-101.5^{\circ}$ ; Co,  $1490^{\circ}$ ; Cr,  $1520^{\circ}$ ; Cs,  $26^{\circ}$ ; Cu,  $1084^{\circ}$ ; Fe,  $1530^{\circ}$ ; F,  $-223^{\circ}$ ; Ga,  $30^{\circ}$ ; Ge,  $958^{\circ}$ ; H,  $-259^{\circ}$ ; Hg,  $-39.7^{\circ}$ ; I,  $113.5^{\circ}$ ; In,  $155^{\circ}$ ; Ir,  $2350^{\circ}$ ; K,  $62.4^{\circ}$ ; La,  $810^{\circ}$ ; Li,  $186^{\circ}$ ; Mg,  $651^{\circ}$ ; Mn,  $1210^{\circ}$ ; Mo,  $2410^{\circ}$  (?); N,  $-210^{\circ}$ ; Na,  $97.5^{\circ}$ ; Nb,  $1700^{\circ}$  (?); Nd,  $840^{\circ}$ ; Ni,  $1452^{\circ}$ ; O,  $-218^{\circ}$ ; Os,  $2700^{\circ}$  (?); P,  $930^{\circ}$ ; Pb,  $327.4^{\circ}$ ; Pd,  $1545^{\circ}$ ; Pr,  $940^{\circ}$  (?); Pt,  $1760^{\circ}$ ; Ra,  $700^{\circ}$ ; Rb,  $38^{\circ}$ ; Rh,  $1960^{\circ}$ ; Ru,  $2450^{\circ}$  (?); S,  $119.2^{\circ}$ ; Sa,  $1300^{\circ}$ ; Sb,  $630^{\circ}$ ; Se,  $217^{\circ}$ ; Si,  $1420^{\circ}$ ; Sr  $<$  Ca  $<$  Ba; Sn,  $232^{\circ}$ ; Ta,  $2800^{\circ}$ ; Te,  $450^{\circ}$ ; Th  $>$  Pt,  $1800^{\circ}$ ; Ti,  $2000^{\circ}$  (?); Tl,  $301^{\circ}$ ; U,  $>1850^{\circ}$ ; V,  $1800^{\circ}$ ; W,  $3030^{\circ}$ ; Y,  $1490^{\circ}$ ; Zn,  $419.4^{\circ}$ ; Zr,  $1700^{\circ}$  (?).

The dependence of the melting point on the position of the element in the periodic system is also graphically illustrated.

H. W.

**Thickness of the Capillary Layer between the Homogeneous Liquid and Vapour Phases, particularly for Carbon Dioxide.** G. BAKKER (*Ann. Physik*, 1920, [iv], 61, 273—302. Compare A., 1919, ii, 12; this vol., ii, 19).—A theoretical paper, in which the thermodynamic equation  $(E_1 - E_2)/2 - E_3 = T^2 \{d(H/\xi T)/dT\}$  is deduced by two methods:  $H$  is the surface tension,  $\xi$  the thickness of the capillary layer,  $T$  the absolute temperature, and  $E_1$ ,  $E_2$ , and  $E_3$  are the energy densities (energy per unit volume) of the liquid, vapour, and unstable phases respectively. The thermodynamic potential of the unstable phase has the same value as the homogeneous liquid and vapour phases. Making use of the formulæ of Gauss—van der Waals and Mills, the relative thicknesses are calculated for the capillary layer of carbon dioxide:  $-25^{\circ}$ ,  $1.52 \mu\mu$ ;  $-10^{\circ}$ ,  $1.51 \mu\mu$ ;  $0^{\circ}$ ,  $1.87 \mu\mu$ ;  $10^{\circ}$ ,  $2.13 \mu\mu$ ;  $20^{\circ}$ ,  $3.11 \mu\mu$ ;  $28^{\circ}$ ,  $5.86 \mu\mu$ ;  $30^{\circ}$ ,  $13.66 \mu\mu$ ; and  $31.12^{\circ}$ ,  $193 \mu\mu$ . Mak-

ing use of a different method of calculation, the values for the number of layers in the capillary layer  $R$  and the total number of layers  $n$  of gas and liquid which form the capillary layer are calculated. For carbon dioxide the values are:

$t$	=	-25°	-10°	0°	10°	20°	28°.
$R$	=	3.0	3.6	4.2	5.1	7.0	11.4
$n$	=	2.7	3.4	4.0	4.9	6.9	11.3
$\zeta$	=	1.6	2.0	2.3	2.8	3.2	6.1 $\mu\mu$ .

The value of  $R$  has also been calculated for benzene and ether. These are based on the van der Waals's equation of state, and are as follows: (1) benzene, 5.4°, 2.4; 50°, 3; 100°, 3.4; 150°, 3.5; 200°, 4.0; 250°, 10.8; and 280°, 16; (2) ether, 0°, 2.4; 20°, 3.3; 50°, 3.3; 80°, 4.2; 120°, 5; 170°, 7.8; 190°, 16.4; and 193°, 21.5.

J. F. S.

**Certain Binary and Ternary Mixtures of Liquids having Constant Boiling Points.** WILLIAM RINGROSE GELSTON ATKINS (T., 1920, 117, 218—220).

**Brown's Formula for Distillation.** SYDNEY YOUNG (*Sci. Proc. Roy. Dubl. Soc.*, 1920, 15, 667—672).—Brown's formula,  $M'_A/M'_B = c \cdot M_A/M_B$  (where  $M'_A$ ,  $M'_B$ , and  $M_A$ ,  $M_B$  are the relative number of molecules of  $A$  and  $B$  in the vapour and liquid phase respectively, and  $c$  is a constant depending on the relative vapour pressures of the pure substances at the boiling point of the mixture), is applicable without serious error to mixtures of benzene and toluene, of which the vapour pressure  $P$  approximately equals  $MP_A + (1-M)P_B$ ,  $P_A$  and  $P_B$  being the vapour pressures of the two pure substances at the same temperature, and  $M$  the molar fraction of the substance  $A$ . Further, for benzene and toluene the best value of the constant  $c$  differs but slightly from the ratio  $P_A/P_B$ , namely, 2.591.

G. F. M.

**Thermodynamics and Probability.** A. BERTHOUD (*J. Chim. Phys.*, 1919, 17, 589—624).—A mathematical discussion of the relationship between entropy and probability, in which a formula is given by means of which it is possible (1) to determine the most probable distribution of the molecules of a monatomic or diatomic gas, according to their velocity or energy, this distribution being expressed by the generalised Maxwell formula; (2) to find the relationship which expresses the entropy of a monatomic or diatomic gas in terms of its temperature and its volume, this relationship agreeing with the thermodynamic expression of entropy. W. G.

**Free Energy and the Hypothesis of Nernst.** A. BOUTARIC (*Le Radium*, 1919, 11, 257—262, 298—305, 348—356).—The author directs attention to the well-known looseness of terminology of writers on the free energy equation,  $A - U = T(dA/dT)$ . He deduces

this, and numerous other equations, by familiar methods, and considers their application to some special examples. J. R. P.

**Heats of Dilution of Certain Aqueous Salt Solutions.**

ALLEN EDWIN STEARN and G. MCP. SMITH (*J. Amer. Chem. Soc.*, 1920, **42**, 18—32).—The reversible molecular heat of dilution has been determined for the chlorides of sodium, potassium, and strontium at various concentrations ranging from 3·2 weight *N* to 0·2 weight *N*, and also for solutions of mixtures of pairs of the above-named salts in equivalent and molecular quantities. The heats of dilution of sodium and potassium chlorides are negative. This fact in the light of the equation  $L_D = RT^2 \cdot (d \log_e p/p_0)/dT$ , in which  $L_D$  is the molecular heat of dilution, indicates an increase in the degree of ionisation with temperature, which is contrary to the experimental results of Noyes (*A.*, 1912, ii, 526), unless they are explained on the basis of decomposition of complexes which exist in solution, but are decomposed on dilution. The heats of dilution for the solutions of mixed salts bear no simple additive relation to the heat effects of the single components at equivalent concentrations. The results are explained on the basis of higher order compounds as put forward by Werner. J. F. S.

**Heats of Dilution of Solutions of Barium Chloride and Barium-Sodium Chloride Mixture.**

G. MCP. SMITH, ALLEN E. STEARN, and R. F. SCHNEIDER (*J. Amer. Chem. Soc.*, 1920, **42**, 32—36. Compare preceding abstract).—The reversible molecular heat of dilution has been determined for solutions of barium chloride of 3·2, 2·8, and 1·6 weight *N*, and for solutions of the mixed salts in equivalent proportions of 3·2, 1·6, 0·8, and 0·4 weight *N*. It is shown that the heat of dilution of the mixture of salts bears no simple additive relationship to the heat of dilution of the components at equivalent dilutions. The behaviour of barium chloride in this respect is therefore analogous to that of strontium chloride (*loc. cit.*). The experimental results can be explained on the same basis as the results obtained with the mixed strontium salts, namely, on the assumption of the formation of compounds of a higher order. J. F. S.

**Relations between Relative Densities, Absolute Density, and Apparent Weight of Solutions.**

O. CHÉNEAU (*Bull. Assoc. Chim. Sucr.*, 1919, **37**, 175—181).—For the interconversion of specific gravity results at 15°, from one basis of reference to another, a table has been compiled showing absolute densities (that is, 15° in vacuum/water at 4° in vacuum), and, in parallel columns, the corrections to be added or subtracted to arrive at corresponding values referred to any of the following bases: 15° in air/water at 15° in air, 15° in vacuum/water at 15° in vacuum, 15° in vacuum/water at 15·5° in vacuum, and 15° in air/water at 4° in vacuum. The values are given to five places of decimals, and range from 0·7 to 1·8. J. H. L.

**Investigation of Mewes' Law of the Relation between the Volume of a Gas and the Temperature.** RUDOLF MEWES (*Zeitsch. Sauerstoff. Stickstoff. Ind.*, 1919, **11**, 73—75, 91—93; from *Chem. Zentr.*, 1920, **i**, 104, 278. Compare Mewes and Neumann, A., 1919, **ii**, 493).—(a) The errors observed in the previous experiments are to be ascribed, in part, to the presence of impurities and consequent liquefaction.

In the second paper the author shows that Landolt's expression,  $(n_{ip} - 1) : (n_{0.760} - 1) = d_{ip}$ , is valid for low temperatures if errors due to partial condensation of the gas by surface action and partial liquefaction are eliminated. H. W.

**Electrical Nature of the Cohesive Forces of Solid Substances.** M. BORN (*Ann. Physik*, 1920, [iv], **61**, 87—106).—A mathematical paper in which relationships are deduced for the molecular forces existing in crystals of the alkali haloids. It was shown by Born and Landé (A., 1919, **ii**, 188) that the compressibility of these salts can be explained by the assumption that the ions exercise attractive and repulsive forces on one another in the sense of Coulomb's law, and that two ions exercise a repulsive force the potential of which is inversely proportional to the ninth power of the distance between the ions. The present calculations are based on this assumption. J. F. S.

**Surface Tension of Mixtures of Water and Alcohol.** JAMES BRIERLEY FIRTH (T., 1920, **117**, 268—271).

**The Adhesion of Starch at Fluid Surfaces. I. Experiments with Starch Grains.** F. B. HOFMANN (*Pflüger's Archiv*, 1917, **167**, 267—279; from *Physiol. Abstr.*, 1917, **2**, 541).—Potato-starch has been used to study the adhesion of solids when distributed between two immiscible liquids, and the conditions which influence this adhesion. J. C. D.

**The Viscosity of Cæsium Salts in Glycerol-Water Mixtures.** P. B. DAVIS (*Carnegie Inst. Pub.*, 1918, **260**, 97—98).—An extension of previous studies by Jones and others on the viscosity of solutions in glycerol and in binary mixtures containing glycerol, with special reference to those salts known to decrease the viscosity of water and of glycerol. Rubidium and cæsium iodides produced phenomenal lowering of the viscosity of glycerol. In these experiments the viscosities of cæsium nitrate and cæsium chloride were measured at 25° and 35°. Cæsium salts decrease the viscosity of glycerol-water mixtures more than rubidium salts. When salts of both rubidium and cæsium increase the solvent viscosity, as, for example, water and acetone or water and the alcohols, the cæsium salt produces a smaller increment than the rubidium salt. CHEMICAL ABSTRACTS.

**The Sorption of Hydrogen by Palladium at Low Temperatures.** JAMES BRIERLEY FIRTH (T., 1920, **117**, 171—183).

**The Effect of Heating on the Absorptive Power of Sugar-charcoal for Sulphur Dioxide.** RAMSAY MIDDLETON WINTER and HERBERT BRERETON BAKER (T., 1920, 117, 319—321).

**Influence of Temperature on the Adsorbability, the Colloid-precipitating Power of some Narcotics.** R. BIERICH (*Pflüger's Archiv*, 1919, 174, 202—217; from *Physiol. Abstr.*, 1919, 4, 184).—The observation of Meyer and Overton of the partition-coefficients between oil and water was confirmed for the partition between cod-liver oil and water in the case of salicylamide and benzamide. The adsorption of narcotics by animal charcoal was found to be almost unaffected by alteration of temperature. In the investigation of the colloid-precipitating power it was found that with isobutyl alcohol, ethylurethane, propylurethane, benzamide, and salicylamide the precipitation of serum albumin by cobalt chloride is strengthened more at high than at low temperatures; the same applied for some of the narcotics with the sodium chloride precipitation of colloidal ferric hydroxide. The narcotic power as tested on tadpoles was always increased by rise of temperature. As regards benzamide and salicylamide this is opposed to the observation of Meyer that the threshold strength of the narcotic varies in the opposite direction to the oil-water partition-coefficient.  
J. C. D.

**Adsorption by Precipitates. II.** HARRY B. WEISER and EDMUND B. MIDDLETON (*J. Physical Chem.*, 1920, 24, 30—73. Compare A., 1919, ii, 269).—The amount of adsorption of phosphate, citrate, tartrate, oxalate, sulphate, iodate, and dichromate ions by definite quantities of precipitated ferric oxide from a ferric oxide sol has been determined. It is shown that since the first process in the precipitation of a colloid by an electrolyte is the neutralisation of the charge by the adsorption of an ion of opposite charge, it follows that two adsorbing media are concerned in the process: the electrically charged particles and the electrically neutral particles. Accordingly, the total amount of a given ion carried down by a precipitated colloid is determined by (a) the adsorption by the electrically charged particles during the process of neutralisation, and (b) the adsorption of the electrically neutral particles during the process of agglomeration and settling. The failure to take the second cause into consideration has led to the erroneous conclusion that the amounts of all precipitating ions carried down by a precipitated colloid are equivalent. The adsorption of equivalent amounts of precipitating ions will neutralise a given amount of colloid, provided the stabilising effect of the ion having the same charge as the colloid is kept constant; but the amounts adsorbed by the neutralised particles will vary with the nature of the adsorbing medium, the nature of the adsorbed ion, and the concentration of the ion in the solution. The determination of adsorption values at the precipitation concentration, as a rule, will not give comparable results because of the variability in



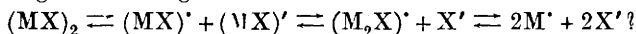
the latter, and the consequent variability in the degree of saturation of the adsorbent in the adsorbed phase. The variations from strict equivalence in the adsorption values of Freundlich are probably due quite as much to the varying concentration and adsorbability of the ions as to the analytical errors. The ions mentioned above are strongly adsorbed by hydrated ferric oxide. The adsorption of univalent ions was relatively weak, so that the precipitate was readily peptised by washing. The amounts of the ions adsorbed are not even approximately equivalent. The phosphate ion is most strongly adsorbed, and the others follow the order: phosphate > citrate > tartrate > oxalate > sulphate > iodate > dichromate. The order of adsorption determined by analysis is entirely different from the order deduced from precipitation values on the assumption that the most strongly adsorbed ion precipitates in the lowest concentration. The latter order is: dichromate > tartrate > sulphate > citrate > oxalate > iodate > phosphate. In addition to the effect of the valency and the adsorbability of precipitating ions, the precipitating values are influenced by differences in the degree of ionisation of electrolytes, the hydrolysis of certain salts, the stabilising effect of the ion having the same charge as the colloid, the mobility of the ions which in certain cases decreases with dilution owing to increased hydration, the rate of coagulation, and the method of determining the critical concentrations. The order of precipitation values is the same for the acids as for their potassium salts except that the former precipitate in somewhat higher concentration than the latter owing to the stabilising effect of the strongly adsorbed hydrogen ion. There is apparently no connexion between the precipitation values and the ionisation constants of the acids investigated, probably because precipitation takes place at such small concentrations (0.0002—0.0008*N*). The order of precipitation values of the potassium salts is: ferrocyanide < ferricyanide < dichromate < tartrate < sulphate < oxalate < chromate < iodate < bromate < thiocyanate < chloride < chlorate < nitrate < bromide < iodide < formate. There is a tendency for ions of the highest valency to be most strongly adsorbed. That there are exceptions to this rule and that ions of the same valency are frequently adsorbed in widely varying amounts may be expected, since adsorbability is a specific property of the ions. J. F. S.

#### Attempt to Extend Planck's Theory of Dilute Solutions.

P. BOEDKE (*Ann. Physik.* 1920, [iv], **61**, 334—352).—A theoretical paper in which Planck's thermodynamical function is considered in connexion with binary liquid mixtures with the object of obtaining expressions which shall represent the equilibrium conditions of such liquid pairs and give the saturation conditions. [See also Jahn, A., 1902, ii, 597.] J. F. S.

**Polymerism of Dissolved Binary Salts.** P. WALDEN (*Zeitsch. Elektrochem.*, 1920, **26**, 60—65).—The molecular weight of a number of binary salts has been determined by the cryoscopic

method at a series of concentrations in non-ionising solvents. As solvents, acetic acid, naphthalene, and diphenylamine were used, and as dissolved substances, tetra-amylammonium iodide, triphenyl-amylphosphonium iodide, tetrapropylammonium iodide, ammonium thiocyanate, tetramethylammonium thiocyanate, tetraethylammonium bromide, ethylammonium chloride, and tetraethylammonium iodide. From the results it is shown that depolymerisation occurs according to the expression  $x = c^{\frac{1}{2}} \cdot \text{const.}$ , that is, the degree of association is directly proportional to the linear concentration or to the distance between the molecules. The molecular weight,  $M$ , of the dissolved salt conditions the dimensions of the constant, since  $x = 0.305M^{\frac{1}{2}}/V^{\frac{1}{2}}$  or  $x = 0.305M^{\frac{1}{2}}/C^{\frac{1}{2}}$ . The influence of the nature of the solvent is shown by the fact that the degree of association  $x$  is inversely proportional to the dielectric constant  $E$  of the solvent, as shown by the expression  $x = 1.92\sqrt{M}/EV^{\frac{1}{2}}$  or  $x = 1.92 \cdot M^{\frac{1}{2}}C^{\frac{1}{2}}/E$ . In view of the influence of the dielectric constant in the depolymerisation, the author puts forward the question: Are the products of depolymerisation oppositely electrically charged according to the scheme:



J. F. S.

**Influence of the Molecular Size of Electrolytes on the Conductivity and the Ionic Velocity of the Ions: Solvation of Ions in Non-aqueous Solutions.** P. WALDEN (*Zeitsch. Elektrochem.*, 1920, 26, 65—71).

—It is shown that a large number of binary salts, mainly iodides, in a number of non-aqueous solvents follow the relationship  $\lambda_{\infty} \eta_{\infty} \sqrt{M} = \text{const.} = 11.15$ , where  $\lambda_{\infty}$  is the limiting conductivity of a salt with molecular weight  $M$  in the solvent under investigation, and  $\eta_{\infty}$  is the viscosity of the solvent. If these salts are regarded as normal, that is, neither associated nor solvated, it becomes possible to determine the degree of solvation of other salts with a fair degree of accuracy. As a control of the values obtained from the formula deduced by Herzog from Einstein's relationship (A., 1911, ii, 23),  $\lambda_{\infty} \eta_{\infty} V^{\frac{1}{2}} = \text{const.}$  may be used. Both equations give solvation values which are practically identical for the ions examined.

J. F. S.

**Is the Migration Velocity of the Ions of an Electrolyte Extremely Large when the Solvent is Capable of Forming Similar Ions?** P. WALDEN (*Zeitsch. Elektrochem.*, 1920, 26, 72—76).

—A theoretical paper in which the conductivity and mobility of the ions of salts, which furnish one ion similar to one of the ions of the solvent, have been considered. The solvents considered are pyridine, formic acid, acetic acid, aniline, *m*-chloro-aniline, nitromethane, methyl thiocyanate, hydrocyanic acid, ammonia, formamide, and nitric acid. The results show that the titular question is to be answered in the negative, and that if there is any influence of the solvent on the dissolved substance in this respect, it only occurs in a few exceptional cases.

J. F. S.

**Dissociating Powers of Free and Combined Water.**

G. FRED ORDEMAN (*Carnegie Inst. Pub.*, 1918, 260, 119—127).—The conductivities of two isohydric solutions were measured, and the measurements repeated after the addition of a third salt (in three different concentrations). The following series of salts were used: (a) isohydric solutions of *M*-potassium chloride and 0.695*M*-calcium chloride, before and after the addition of sodium, potassium, ammonium, magnesium, calcium, or strontium chloride; (b) isohydric solutions of *M*-sodium chloride and 0.597*M*-calcium chloride, the addendum being sodium, ammonium, magnesium, calcium or strontium chloride, or potassium nitrate; (c) isohydric solutions of *M*-sodium nitrate and 0.681*M*-calcium nitrate, the addendum being sodium, potassium, ammonium, magnesium or calcium nitrate, or potassium chloride; (d) isohydric solutions of 0.5*M*-sodium nitrate and 0.310*M*-calcium nitrate, the addendum being as in (c); (e) isohydric solutions of *M*-potassium nitrate and 0.698*M*-calcium nitrate, the addendum being sodium, potassium or strontium nitrate, or potassium or sodium chloride. For every pair of solutions, the suppression of the conductivity is more pronounced in the hydrated solutions, showing that the added salt dissociates more in the non-hydrated solutions than in the comparable, isohydric solutions of the hydrated salts. The repression of the ionisation of the hydrated salts added is much greater than that of comparable quantities of non-hydrated salts in both isohydric solutions of every pair studied. A few added salts, having no common ion, show irregular results. The combined water (of hydration) in the solution of a hydrated salt is assumed to possess less ionising power than the uncombined water, hence the salt added would be less dissociated. The hydrated salts used as addenda are less dissociated than the other addenda, because the water of hydration now exists in both of any pair of solutions. The dissociation, however, is always less in the solution of the hydrated salt of any pair, because of the smaller dissociating power of the water of hydration already present in that solution.

CHEMICAL ABSTRACTS.

**The Ultimate Structure of Isomorphous Substances.**

F. RINNE (*Centr. Min.*, 1919, 161—172).—From the results of the X-ray analysis of the crystal structure of a number of substances, the author has calculated the absolute atomic or molecular volumes of the substances comprising a number of isomorphous series. The substances dealt with are the cubic elements aluminium, copper, silver, gold, and lead, the rhombohedral carbonates of magnesium, calcium, manganese, iron, zinc, and cadmium, and the haloids of lithium, sodium, potassium, rubidium, and caesium. From a comparison of the Röntgen-ray diagrams of a large number of minerals, which are usually isomorphous mixtures, with those of pure substances, it is concluded that there is no essential difference between their structures; that is, the X-ray evidence favours the view that in isomorphous mixtures the dispersity is so great that

it is highly probable that the vicarious constituents replace one another atom for atom or group for group in the lattice structure of the crystal. The importance for isomorphism of the chemical nature, and especially of the valency, of the vicarious atoms or atomic groups is insisted on. This factor is often of more importance in determining isomorphism or miscibility than molecular volume. Thus, in the case of the above elements, although the edge of the fundamental lattice is practically of equal length for aluminium, silver, and gold, and considerably less for copper, silver and gold are perfectly miscible together, but only slightly so with aluminium. In the case of the haloids of the alkali metals, the miscibility varies with the temperature to a much greater extent than would be expected were the dimensions of the fundamental lattices the ruling factor. The author regards the mixed crystal state as one intermediate between a physical mixture and a true chemical compound.

E. H. R.

**Von Weimarn's Theory of the Colloidal State.** E. H. BUCHNER and J. KALFF (*Rec. trav. chim.*, 1920, **39**, 135—144).—The authors consider that von Weimarn's theory of corresponding states in the formation of precipitates is untenable. They show that his law giving the relationship between "the coefficient of precipitation," on which the form of the precipitate depends, the solubility of the substance precipitated, and the amount of the precipitate formed is incorrect in the cases of such precipitates as calcium fluoride, barium fluoride, and calcium sulphate in comparison with barium sulphate, and in the cases of silver chloride, bromide and iodide, and lead iodide. Further, that in the case of such precipitates as aluminium hydroxide, the conditions cannot be expressed by any formula. Whilst his theory may have some value qualitatively, his law of corresponding states is not confirmed by quantitative experiments.

W. G.

**Swelling and Solution of Aleuron.** MARIAN O. HOOKER and MARTIN H. FISCHER (*Kolloid Zeitsch.*, 1920, **26**, 49—58).—The amount of swelling of aleuron (a mixture of plant proteins) occasioned by water, dilute solutions of hydrochloric, nitric, sulphuric, lactic, formic, and tartaric acids, hydrochloric acid mixed with various quantities of the chlorides of sodium, potassium, iron, aluminium, ammonium, copper, magnesium, calcium, and strontium respectively; hydrochloric acid mixed with potassium bromide, nitrate, iodide, acetate, thiocyanate, tartrate, and citrate respectively; and hydrochloric acid mixed with carbamide, methyl alcohol, ethyl alcohol, dextrose, and sucrose respectively, has been measured. The amount of aleuron dissolved by the above-named solutions has also been determined. A similar series of experiments has been carried out with sodium hydroxide solutions and with sodium hydroxide solution to which the above-named substances have been added. It is shown that aleuron behaves, as

regards its swelling and solution, in much the same way as gelatin, fibrin, blood serum, and gluten. It swells more in acid and alkali solutions than in water, but the amount of swelling does not run parallel with hydrogen- or hydroxyl-ion concentration. The swelling is reduced, not only by neutralisation of the acid or alkali, but also by the addition of neutral salts. The greater the concentration of the added salt, the greater the reduction of the swelling. Non-electrolytes do not influence the swelling in either acid or alkali solution. The solubility of aleuron in acids and in alkalis is also greater than in water, but it does not run parallel with the swelling. Some salts increase the solubility, whilst others reduce it in both acid and alkaline solutions, but there is no parallelism between solubility and swelling. The results indicate that hydration and solution of an albuminous substance or mixture of albuminous substances, although often connected and often occurring in the same sense, yet are not identical processes. Each follows its own particular laws.

J. F. S.

**Influence of the Concentration of Electrolytes on some Physical Properties of Colloids and Crystalloids.** JACQUES LOEB (*J. Gen. Physiol.*, 1920, 2, 273—296).—When alkali or neutral salt is added to a 1% solution of sodium gelatinate separated from distilled water by a collodion membrane, the rate of diffusion is diminished. This depressant action is greater when the cation of the added electrolyte is bivalent than when it is univalent. When a neutral  $M/256$ -solution of a salt with univalent cation is separated from distilled water by a collodion membrane, and an alkali or neutral salt is added, the diffusion of water is also depressed in proportion to the amount added. It can be shown that under these conditions water diffuses through the membrane in the form of positively charged particles. In the case of the diffusion of water into a neutral salt with univalent or bivalent cation, the effect of the addition of electrolyte on the rate of diffusion can be explained on the basis of the influence of the ions on the electrification and the rate of diffusion of the electrified particles of water. Since the influence of the addition of electrolyte seems to be the same in the case of solutions of metal gelatinate, the question arises whether this influence cannot also be explained in the same way, and, if this be true, the further question can be raised whether this depressing effect necessarily depends on the colloidal character of the gelatin solution, or whether in both cases the same property of matter is not being dealt with, namely, the influence of ions on the electrification and rate of diffusion of water through a membrane.

The curve representing the influence of the concentration of the electrolyte on the initial rate of diffusion of water from solvent into the solution through the membrane is similar to the curve representing the permanent osmotic pressure of the gelatin solution. The diffusion of water as negatively charged particles into a solution of gelatin chloride is depressed by addition of an acid or

neutral salt. This is also found to be true when the diffusion takes place into a solution of  $M/512\text{-Al}_2\text{Cl}_6$ . J. C. D.

**Influence of a Slight Modification of the Collodion Membrane on the Sign of the Electrification of Water.** JACQUES LOEB (*J. Gen. Physiol.*, 1920, **2**, 255—271).—Collodion membranes which have received one treatment with 1% gelatin solution show for a long time afterwards a different osmotic behaviour from untreated membranes. This difference shows itself only towards solutions of those electrolytes which have a tendency to induce a negative electrification of the water particles diffusing through the membrane. When solutions of salts with tervalent cation are separated from water by collodion membranes treated with gelatin, water diffuses rapidly into the solution, whilst no water diffuses when the collodion membrane has received no gelatin treatment. Solutions of acid separated from water by treated membranes show negative osmosis, whereas with untreated membranes positive osmosis occurs. These differences only occur in that range of concentrations of electrolytes inside of which the forces determining the rate of diffusion of water through the membrane are predominantly electrical, that is, from 0 to about  $M/16$ . The differences in the osmotic behaviour of the two types of membrane are not due to differences in permeability, but are rather due to the fact that water diffuses into solutions of tervalent cations or acids through gelatin-treated membranes as negatively charged particles, whilst in the case of non-treated membranes the charge is positive. Treatment of the membranes with caseinogen, egg-albumin, blood-albumin, or edestin has the same effect, but treatment with peptone from egg-albumin, alanine, or starch has no such effect. J. C. D.

**Colloidal Electrolytes. Soap Solutions and their Constitution.** JAMES W. MCBAIN and C. S. SALMON (*Proc. Roy. Soc.*, 1920, [A], **97**, 44—65; *J. Amer. Chem. Soc.*, 1920, **42**, 426—460).—Colloidal electrolytes are solutions of salts in which an ion has been replaced by a heavily hydrated multivalent micelle carrying an equivalent sum total of electric charges, and also serving as an excellent conductor of electricity. This new class of electrolytes probably includes most organic compounds containing more than eight carbon atoms, and capable of forming ions, also acid and alkali solutions of proteins, dyes, indicators, sulphonates, soaps, alkali tungstates, zincates, tellurates, and silicates. The constitution of solutions of the sodium and potassium salts of behenic, stearic, palmitic, myristic, lauric, decolic, octoic, hexoic and acetic acids has been investigated. The vapour pressure and elevation of the boiling point have been ascertained by the dew-point method for solutions of the above-named salts at concentrations  $0.2N$ — $3.0N$ . From the results, coupled with osmotic and conductivity data previously published (T., 1914, **105**, 435), the concentration of crystalloid constituents and the concentration of colloid constituents are deduced. It is shown that, in  $N$ -solutions,

in every case colloid material is present; in the case of the hexoate, 15% is present as colloid, whilst with potassium stearate, 99% is colloid. The amount of colloid decreases rapidly with decrease in concentration, and it apparently becomes inappreciable with  $N/5$ -laurate solutions. The ionic micelle are regarded as either (in the case of palmitate) an agglomeration of palmitate ions heavily weighted by water as a complex solvate,  $(P')_n \cdot (H_2O)_m$ , or, and more probably, a collection of all, or nearly all, the colloid in the ionic micelle,  $(NaP)_x \cdot (P')_n (H_2O)_m$ .

J. F. S.

**Penetration of Electrolytes into Gels. I. Penetration of Sodium Chloride into Gels of Agar-agar containing Silver Nitrate.** WALTER STILES (*Biochem. J.*, 1920, 14, 58—72).—

The penetration of sodium chloride from solutions of various concentrations ( $5N$ — $0.05N$ ) into agar gels has been followed by the indicator method. When silver nitrate is present in the gel, the entrance of sodium chloride into the gel is marked by the formation of silver chloride, and the progress of the chloride into the gel is indicated by the forward movement of the sharp line of demarcation between the silver chloride in the gel and the unprecipitated silver salt. The distance this line of demarcation has moved forward in any time is termed the penetration. It marks the position of a definite concentration of chloride, namely, the saturation concentration of silver chloride. The penetration of sodium chloride into agar gels containing silver nitrate is, within wider limits, proportional to the square root of the time. If  $P$  is the penetration in a time  $t$ ,  $P/\sqrt{t}$  = constant for any particular gel and any particular concentration of penetrating salt, and is termed the penetration factor. The rate of penetration is dependent on the initial concentration of the penetrating salt, the higher the concentration of the salt the more rapid the penetration. The concentration of the gel itself appears to exercise little influence on the rate of penetration, but, owing to the probability of actions between the silver salt and the gel, and hence doubt as to the true active concentration of the silver salt in the gel, the influence of concentration of the gel must be left an open question. In any case, the influence cannot be great in gels containing between 1 and 4% agar. The expression obtained by von Fürth and Bubanovič (*A.*, 1919, ii, 13) to indicate the relationship between the penetration, time, and concentration of the penetrating salt only holds in very special cases and between narrow limits, and is even then only very approximate. The following more general empirical relationship is deduced,  $P/\sqrt{t} = k \log c + k'$ , where  $c$  is the initial concentration of the penetrating salt,  $k$  a constant depending on the nature of the penetrating salt and also, although to a slight extent, on the nature of the gel content, and  $k'$  a second constant depending mainly on the concentration of silver nitrate in the gel.

J. F. S.

**Adsorptive Stratification in Gels. III.** SAMUEL CLEMENT BRADFORD (*Biochem. J.*, 1920, 14, 29—41. Compare *A.*, 1919, ii, 139).—A discussion of the supersaturation and the adsorption

theory of the Liesegang phenomenon in gels. The author supports the adsorption theory by a number of experimental facts. The formation of bands usually ceases long before the bottom of a tube is reached. The hypotonic reagent is invariably so strong that this effect can only be due to the solute in the gel having been exhausted from the lower regions of the tube. This fact also controverts the deduction from the supersaturation theory, that the diffusion of the solute in the gel is negligible.

With certain colloidal precipitates, such as manganese sulphide, in agar, a tendency is observed to form large spherical aggregates which have much the same structure and density as the bands, except that they frequently show concentric banding. When one of these spherical aggregates begins to form in the zone where a band will shortly appear, the band does not extend to join the sphere, but a spherical cavity, 2—3 mm. wide, is left surrounding the concretion, from which the surface of the cavity is everywhere equidistant. This effect must be due to the solute having been exhausted from the neighbourhood of the aggregate. Its spherical form implies that nutrient material has accrued equally from all directions.

J. F. S.

**Mutual Action of Sols.** WILDER D. BANCROFT (*J. Physical Chem.*, 1920, **24**, 21—29).—A theoretical paper in which it is shown that when positively charged gelatin is mixed with a negatively charged sol, or negatively charged gelatin with a positively charged sol, there may be precipitation over a range of relative concentrations. When two sols, peptised by water, are mixed, the mutual adsorption may decrease the adsorption of water to such an extent that precipitation takes place. There may be, and often is, mutual adsorption when two sols having the same electrical charge are mixed. The mutual adsorption of positively charged ferric oxide and positively charged gelatin in ammonia solution gives a different product from the mutual adsorption of positively charged ferric oxide and positively charged gelatin to which ammonia is subsequently added, inasmuch as in the first case precipitation is brought about, whilst in the second there is no precipitation.

J. F. S.

**[Physical Chemical Analysis of Metal Hydrosols.] An Explanation.** RICHARD ZSIGMONDY (*Kolloid Zeitsch.*, 1920, **26**, 67—69).—Polemical; an answer to Pauli's criticism (this vol., ii, 168) of certain parts of a paper by Varga.

J. F. S.

**Rôle of Valency in the Coagulation of Suspensoids by Electrolytes.** WOLFGANG OSTWALD (*Kolloid Zeitsch.*, 1920, **26**, 69—81. Compare this vol., ii, 168).—The various theories which have been put forward to explain the function of valency in the coagulation of suspensoids are summarised, and the precipitation values of a large number of electrolytes are collected from various sources and tabulated. From the absorption theory of Freundlich,



an expression is deduced which gives a quantitative relationship between valency and precipitating power. This has the form  $1/c_1:1/c_2:1/c_3 \dots = 1:2^n:3^n \dots$ , in which  $c_1$ ,  $c_2$ , and  $c_3$  are the precipitating values of uni-, bi-, and ter-valent electrolytes, and  $n$  is a constant. It is shown that none of the theories hitherto put forward satisfactorily accounts for the coagulation of electrolytes. It is shown that the rôle of valency as the determining factor in coagulation processes has been considerably overestimated. This follows from the facts that (1) the precipitating values of electrolytes of the same valency differ considerably, (2) univalent electrolytes in some cases have smaller precipitating values than bivalent electrolytes, and (3) salts of different valencies fall into the same group with respect to their precipitating values. J. F. S.

**Precipitation of Congo-rubin by Electrolytes.** WOLFGANG OSTWALD (*Koll. chem. Beihefte*, 1920, **26**, 92—102. Compare A., 1919, ii, 187, 400).—A continuation of previous work (*loc. cit.*). It is shown that the behaviour of Congo-rubin toward electrolytes in respect of Schulze's rule is exactly the same as that of inorganic hydrosols. The behaviour of Congo-rubin in respect of its colour changes in the presence of electrolytes is of the same nature and depends on the same causes as the colour changes of inorganic hydrosols, for example, the colour changes of gold sols, or, in other words, the phenomenon is of colloidal chemical character.

J. F. S.

**Equilibria in Solutions containing Mixtures of Salts. The System Water and the Chlorides and Sulphates of Sodium and Magnesium at 25°.** W. C. BLASDALE (*J. Ind. Eng. Chem.*, 1920, **12**, [ii], 164—167).—Previous work on this subject indicates that the solid phases to be expected at 25° are  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NaCl}$ , and  $\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  (blödite). In ascertaining the limits of the fields representing the composition of all the solutions which can be in equilibria with each of the eight solid phases, the composition of solutions saturated with respect to  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{NaCl}$  was determined, and the ends of two axes at right angles, one to represent the relative proportions of  $\text{MgSO}_4$  and  $\text{NaCl}$ , and the other of  $\text{Na}_2\text{SO}_4$  and  $\text{MgCl}_2$ , were fixed. The solubility of each of the former four salts in solutions containing increasing concentrations of a second salt which yields a common ion was determined up to the point at which a second solid phase appeared, and thereby a number of points intermediate between the extremities of the two axes, representing solutions in equilibrium with two solid phases, were fixed. Further, starting with solutions saturated with respect to two solids, the composition of solutions saturated with respect to each pair of solids, in the presence of increasing concentrations of that salt which yielded a fourth ion, was determined up

to the point at which a third solid separated. The results are shown in a curve, in which the horizontal axis is used to represent the number of mols. of  $\text{MgSO}_4$  and  $\text{NaCl}$ , and the vertical axis the number of mols. of  $\text{MgCl}_2$  and  $\text{Na}_2\text{SO}_4$ , per 1000 mols. of water, and tables are given showing the composition of all these solutions which represent critical points. S. S. A.

**Reaction Isochore and Velocity of Reaction from the Statistical Point of View.** M. POLÁNYI (*Zeitsch. Elektrochem.*, 1920, 26, 49—54).—A theoretical paper in which it is shown that the velocity constant of a reaction of the type  $A + B_2 \rightleftharpoons AB + B$  in the endothermic direction is given by the product of the number of collisions and the equilibrium constant, and in the reverse direction it is the same as the number of collisions. These results are deduced from the assumption that it is just as likely after a collision between  $A$  and  $B_2$ , that the particles react, or that they are dispersed without a reaction taking place. The results of the theoretical investigation are tested by means of the experimental results of Bodenstein and Lind on the reaction  $\text{Br} + \text{H}_2 \rightarrow \text{BrH} + \text{H}$  (A., 1907, ii, 76), and found to be in accordance with the experimental facts. J. F. S.

**Influence of Pressure on the Temperature of Explosion.** G. TAMMANN (*Nach. Ges. Wiss. Göttingen*, 1919, 220—224; from *Chem. Zentr.*, 1920, i, 146).—The explosive material is contained in a small glass tube open at one end, and is placed in a steel cylinder filled with mercury; the latter is connected with a spring manometer and pressure pump. The cylinder is heated in an oil-bath provided with an efficient stirrer, the temperature of the bath being observed from minute to minute. Tables are given showing the rate of heating in degrees per ten minutes before attaining the temperature of explosion, the weight of explosive, the pressure and temperature at which explosion occurs, the differences in pressure before and after the explosion, and the sudden rise of pressure during the explosion. The temperature of explosion of moist glyceryl nitrate varied somewhat considerably at constant pressure; increase of the latter by 2500 kilos. per sq. cm. appeared to depress the temperature of explosion by  $8.4^\circ$ , but the variation lies within the limits of experimental error. With dry glyceryl nitrate, the variations are less marked, but a distinct influence of the pressure on the temperature of explosion is not observed; a similar effect is still less certain in the case of a mixture of tetranitromethane (2 mols.) and benzene (1 mol.). With tetranitromethane (2 mols.) and naphthalene (1 mol.), an increase in pressure of about 2000 kilos per sq. cm. causes an elevation of  $5.7^\circ$  in the temperature of explosion. The influence of pressure on the temperature of explosion of liquid explosives is determined by the effect of pressure on the conductivity for heat of the material itself and its environment, and by alteration in the chemical-kinetic conditions, such as the increase in the number of molecular collisions caused by

isothermal increase in pressure as a consequence of the increase in volume of the explosive.  
H. W.

**Difference in Chemical Activity of Free and Semi-combined Water as Illustrated by the Effect of Neutral Salts on the Hydrolysis of Acetic Anhydride.** GERALD C. CONNOLLY (*Carnegie Inst. Pub.*, 1918, **260**, 131—143).—In extension of the work of Holmes and Jones (*ibid.*, 1915, **230**) on the effect of salts on the hydrolysis of methyl acetate and methyl formate, the action of strongly hydrated and of slightly hydrated salts on the hydrolysis of acetic anhydride has been studied with the object of determining whether any chemical difference exists between free and combined water. Care being taken always to keep the water content constant,  $M$ -,  $0.5M$ -, and  $0.25M$ -solutions of various salts (potassium, sodium, calcium, magnesium, barium, and strontium chlorides, sodium and magnesium sulphates, potassium and sodium nitrates) at  $15^\circ$  and at  $25^\circ$  were treated with acetic anhydride, aliquot portions were removed at various intervals, and the acetic acid estimated. The amount of acetic acid present in mixtures of the acid and its anhydride was estimated by adding aniline and titrating the total acetic acid with sodium hydroxide. The concentration of the anhydride was 5%, and in no case did the time exceed sixty minutes at  $15^\circ$  and forty minutes at  $25^\circ$ , since the hydrolysis by water was practically complete.

All the salts examined, excepting sodium and magnesium sulphates, have in the case of the greater concentrations a retarding influence on the hydrolysis, the retardation diminishing with increasing salt dilution. The four non-hydrated salts have practically the same retarding effect on the hydrolysis. The hydrated salts, excepting magnesium chloride, produce greater hydrolysis than the non-hydrated salts, and with the more dilute solutions there is an appreciable acceleration of the hydrolysis of the anhydride over that due to water alone. Sodium and magnesium sulphates at all concentrations have a marked accelerating effect on the hydrolysis. Calcium, strontium, and barium chlorides also exert an accelerating influence in the more dilute solutions. The results with magnesium chloride and sulphate were inconclusive, the former resembling the non-hydrated salts in retarding the hydrolysis at all dilutions.

CHEMICAL ABSTRACTS.

**The Alkaline Hydrolysis of Tartaric Ester.** ANTON SKRABAL and ERNA SINGER (*Monatsh.*, 1919, **40**, 363—375).—The rate of hydrolysis of methyl tartrate by a mixture of sodium carbonate and sodium hydrogen carbonate has been measured, after the procedure necessary for the attainment of satisfactory results had been worked out in the case of methyl acetate. Referred to  $[\text{OH}]'=1$  and at  $25^\circ$ , the constants for the first and second stages in the hydrolysis of methyl tartrate are  $k_1=206$  and  $k_2=14.7$  respectively, whilst for methyl acetate  $k=5.4$ .

J. K.

**Catalysis of Hydrogen and Oxygen Mixtures at the Ordinary Temperature by Moistened Contact Substances. II. The Platinum Metals as Hydrogen Carriers.** K. A. HOFMANN and LOTTE ZIFFEL (*Ber.*, 1920, **53**, [B], 298—314. Compare Hofmann and Ebert, A., 1917, ii, 25).—The results may be summarised in the following manner.

Mixtures of oxygen and hydrogen are catalysed at palladium, platinum, or iridium surfaces at very different rates, depending on the exact extent, at the moment, to which they are charged with gas. Pre-treatment with oxygen is thirty to fifty times as effective in the case of palladium, three times with platinum, and three to ten times with iridium as is pre-treatment with hydrogen. The greater activity caused by charging with oxygen is not brought about by the adsorbed or occluded gas serving as a source for the formation of water, since the amount of metal required for catalysis is insufficient to produce this effect, but depends on the production of a "fresh" hydrogen-metal combination, which, in the cases of palladium and platinum, is far more active than an "aged" preparation. The catalyst shows greater activity in proportion as this "fresh" condition is more rapidly and completely developed. In the case of iridium, another factor is involved, since the metal, in presence of gases containing excess of oxygen, can function as an active oxygen electrode.

The close parallelism between catalytic and electromotive activity indicates that both effects are to be ascribed to the same cause. This probably depends on the presence of free or metallically-dissolved hydrogen atoms, which cause the hydrogen potential and ultimately combine with the oxygen of the gas mixture to form water. Under the experimental conditions adopted, an active oxygen electrode is only formed with finely divided iridium when the oxygen concentration is high; platinum and palladium behave entirely as hydrogen electrodes.

The maximal velocity of formation of water is not invariably observed when the gases are used in the proportion of hydrogen (2 vols.) to oxygen (1 vol.), but, according to conditions, may occur at a greater or smaller oxygen concentration, according as the catalyst becomes more or less rapidly saturated with hydrogen. If the catalyst can also function as an oxygen electrode, as in the case of finely-divided iridium, a second maximum may occur with a higher oxygen content in the gas.

It may be generally stated that the surface does not show its greatest catalytic activity when hydrogen and oxygen are absorbed according to the measure of their combination at an electrically neutral electrode, but that the maximum possible hydrogen or oxygen potential must be "freshly" developed in order to react with the gaseous mixture at the maximum rate. H. W.

**A Relation among the Atomic Weights of Chemical Elements.** SUMINOSUKE ONO (*Proc. Phys. Math. Soc. Japan*, 1919, [3], **1**, 231—236).—The atomic weight ( $A$ ) may be given by a

formula,  $A = N'^{\eta}$ , where  $\eta = 1.204$  and  $N'$  is roughly equal to Moseley's atomic number + 2 or Rydberg's ordinals. For the more exact calculation of the atomic weight,  $N'^{\eta}$  may become a more complicated function, and  $N'$  may be identical with neither the atomic numbers nor the ordinals.

CHEMICAL ABSTRACTS.

**The Derivation of Molecular and Atomic Weights from Vapour Densities in Chemical Teaching.** W. MANCHOT (*Chem. Zeit.*, 1920, **44**, 153—154).—An academic discussion on the most suitable formulæ for expressing the relation between molecular weights and gas densities with respect to water, air, and hydrogen in teaching chemistry.

E. H. R.

**The Law of the Harmonic Triangle in Chemical Reactions.** EDUARD SCHMIZ (*Ber. Deut. pharm. Ges.*, 1920, **30**, 27—33).—The numerical relationships shown in a previous paper to hold between the atomic weights of a number of the elements (A., 1919, ii, 460) are now shown to hold also between the atomic and molecular weights of substances taking part in simple inorganic reactions. These relationships are those holding between the sides and hypotenuse of an isosceles right-angled triangle, the radius of the inscribed circle and that of the circle circumscribed about the squares erected on the sides of the triangle. It is claimed that, in simple cases, unless such a relationship holds between the molecular weights of substances, interaction between them cannot take place.

E. H. R.

**Structure of the Atomic Nucleus.** E. GEHRCKE (*Ber. Deut. physikal. Ges.*, 1919, **21**, 779—784).—A theoretical paper in which the author formulates the constitution of the nucleus of the helium, lithium, glucinum, boron, nitrogen, and carbon atoms. The helium nucleus consists of two electrons and four hydrogen ions. In the case of lithium, the nucleus consists of four electrons situated at the corners of a regular tetrahedron, and seven hydrogen ions situated one at the centre of gravity of the tetrahedron, one at each corner of the tetrahedron, and two in an orbit close to the tetrahedron and at some distance from the outer electron ring. This nucleus is capable of accounting for the doublet series of the lithium spectrum. Glucinum possesses a nucleus consisting of five electrons situated one at the centre of gravity and one at each of the corners of a regular tetrahedron, and nine hydrogen ions situated one in the middle of each of the edges of the tetrahedron and the remaining three in an orbit surrounding the tetrahedron. This nucleus is capable of explaining triplet series of the glucinum spectrum. Boron has a nucleus composed of six electrons situated one in the middle of each of the edges of a regular tetrahedron, and eleven hydrogen ions situated one at the centre of gravity of the whole, one on the outside of each of the nuclear electrons, and one at each of the corners of the tetrahedron. The nucleus of carbon consists of six electrons situated as in the case of boron, one in

the middle of each of the edges of a regular tetrahedron, and twelve hydrogen ions, two of which are attached to each of the electrons. A nucleus so constructed accounts for the tetrahedral directions of the carbon valencies, since it will possess four electrostatic lines of force in these directions. Nitrogen is regarded as having a nucleus composed of seven electrons and fourteen hydrogen ions, which are grouped into three helium nuclei in an orbit surrounding one electron with two hydrogen ions attached to it. Constructing, further, after the manner of nitrogen, the nucleus oxygen is regarded as a ring of four helium nuclei, fluorine as four helium nuclei in a ring round an  $H_3^+$  ion, and neon as a ring of four helium nuclei round a single helium nucleus. J. F. S.

### Condition of Dissociation of the Gases of the Fixed Stars.

JOHN EGGERT (*Physikal. Zeitsch.*, 1919, **20**, 570—574).—A theoretical paper in which, on the basis of the Nernst heat theorem, the relationship between the dimensions of the chemical constants deduced by Sackur, Tetrode, and Stern, and the Bohr atomic theory, the degree of dissociation of the atoms into nucleus and electrons, possible at temperatures between  $10^6$  and  $10^{70}$  and pressures of  $10^7$  atm., is investigated. The calculations show that, considering only one type of atomic model, the maximum dissociation would consist in the separation of the two outermost rings of electrons, that is, of sixteen electrons. From this, it follows that the mean atomic weight of the gases of the fixed stars is 3.3, a value which is very near that (2.8) deduced by Eddington in his theory of the structure of the fixed stars. J. F. S.

**Atomic Nuclei and  $\alpha$ -Radiation.** HANS TH. WOLFF (*Ann. Physik*, 1919, [iv], **60**, 685—700).—A theoretical paper in which a theory of the structure of the atomic nucleus and the forces operative in the nucleus is put forward. The nucleus has a disk-like form and is made up of concentric rings. With the exception of the outermost ring, they consist of singly charged hydrogen atoms and doubly charged helium atoms, which are rotating round the middle point. Outside these charged atoms in the outermost ring, rotate the electrons. The positive charges are assumed to exert an attraction on one another when they are at certain distances apart, and thereby effect the stability of the nucleus. At small distances, however, a repulsive force becomes operative. On this assumption, it is shown that one of the two potential formulæ,

$$P = L(1/R - A_2/R^2 + A_3/R^3)$$

and  $P = L(1/R - A_3/R^3 + A_5/R^5)$ , represents the reciprocal action of the positive charges in the atomic nucleus. Expressions are deduced for calculating the potential and field of force which a rotating charge will generate in a point in the same plane, but in a ring outside itself. The conditions of stability after movement are worked out for a point which attracts a rotating charge according to either of the above formulæ. Both potential formulæ are applied to the atomic nucleus of the radium atom, and the constants

determined so that they are in keeping with the expulsion of an  $\alpha$ -radiation of the experimentally determined velocity.

J. F. S.

**Analysis of an Electron-transference Hypothesis of Chemical Valency and Combination.** JOHN MARSHALL (*Proc. Roy. Soc. Edin.*, 1919, **39**, [3], 209—233).—A mathematical investigation of refractive indices based on the Thomson model atom, in which account is taken of the effect of the positive electrification as well as of the electrons, and of the fields of electrical action between the atoms of a molecule. The results are in moderate agreement with experiment.

J. R. P.

**The Octet Theory of Valence and its Applications with Special Reference to Organic Nitrogen Compounds.** IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1920, **42**, 274—292).—The octet theory of valence, which has been described in previous papers (Lewis, A., 1916, ii, 310; Langmuir, A., 1919, ii, 506), is here applied particularly to organic nitrogen compounds, although the general application of the theory to inorganic nitrogen compounds and to salts is discussed.

The number of available electrons in the outside shell of any atom is usually given by the ordinal number of the column of the periodic table in which the element is found. The number, which may be represented by  $E$ , corresponds with the maximum positive valence of the ordinary valence theory, and is one for sodium, four for carbon, five for nitrogen, six for oxygen, and seven for chlorine. It is readily proved that the octet theory is entirely in agreement with the ordinary valence theory whenever the ordinary formulæ are based on valences of unity for hydrogen and  $8-E$  for each other element. Thus the ordinary formulæ agree with those of the octet theory whenever the following valences are adopted: hydrogen, one; carbon, four; nitrogen and phosphorus, three; oxygen and sulphur, two; chlorine, bromine, etc., one. On the other hand, all formulæ in which valencies different from these have been used require modification according to the octet theory. The application of the octet theory to the following compounds, among others, the formulæ of which require modification, is particularly discussed: sodium chloride,  $\text{Na}^+\text{Cl}^-$  (the co-valence of both atoms is zero); ammonium chloride,  $(\text{NH}_4)^+\text{Cl}^-$  (the nitrogen is quadricovalent); triphenylmethyltetramethyl ammonium,  $(\text{NMe}_4)^+[\text{CPh}_3]^-$  (the nitrogen is quadricovalent, whilst the central carbon atom in the anion is tercovalent); diazophenol,  $\text{R}-\text{N} \begin{smallmatrix} \text{O} \\ \diagup \end{smallmatrix} \text{N} \begin{smallmatrix} \diagdown \\ \text{N} \end{smallmatrix}$ ; diazonium compounds,  $(\text{R}-\text{N} \equiv \text{N})^+\text{OH}^-$  or  $\text{R}-\text{N} \equiv \text{N} \cdot \text{OH}$ ; triazo-compounds,  $\text{R}-\text{N} = \text{N} = \text{N}$ ; hydroxylamine,  $\text{H}_2\text{N} \cdot \text{OH}$  or  $\text{H}_3\text{N}-\text{O}$ .

According to this theory, all salts are completely ionised even before they are brought into solution. This conclusion is, moreover, in agreement with the recent work of Milner, Ghosh and

others; it explains why there are weak acids and weak bases, but no weak salts.

The known cases of isomerism, including stereoisomerism, of nitrogen, phosphorus, and sulphur compounds are in full accord with the octet theory.

The fact that organic cyanates, cyanides, and nitrites exist in two isomeric forms whilst the corresponding inorganic salts exist in only one form is explained, since the multivalent atoms of the metals in the inorganic compounds are not attached to definite atoms of the acid radicles.

The available data on phosphonium, arsonium, sulphonium, and oxonium compounds are in full accord with the octet theory, which gives for these compounds constitutions closely resembling those previously assigned by Werner. H. W.

**Accelerated Filtration through Filter-paper.** G. BRUHNS (*Chem. Zeit.*, 1920, **44**, 207).—A filter-paper, folded in the usual way, is placed in a funnel, and the loose end of the three-fold layer is turned back and pressed against the side of the funnel; this folding back is repeated several times, so that the greater part of the interior of the funnel is covered by only one thickness of paper. In the ordinary way of using a filter, one-half of the funnel is covered by a threefold layer of paper. W. P. S.

**Small Generator for Acetylene Bunsen Burners.** P. ASKENASY (*Zeitsch. Elektrochem.*, 1920, **26**, 32).—An acetylene generator is designed which with one charge of carbide will feed a large bunsen burner with acetylene for six hours. J. F. S.

[**Lecture Experiment.**] **A Chemical Model of the Excitation Process.** MAX VERWORN (*Pflüger's Archiv*, 1917, **167**, 289—308).—A mixture of pure, vacuum-distilled nitric acid and 40% formaldehyde solution possesses considerable lability, and will react with explosive violence by the action of certain stimuli. The reaction is an oxidative decomposition of the formaldehyde to carbon dioxide and water. The mixture will remain unchanged at ordinary temperatures, but on addition of nitrous oxide, colloidal platinum, or on warming there is first a latent period during which no change occurs, which is followed by the violent reaction. Cooling the mixture, or the addition of water, or a carbamide solution will inhibit the process. If the mixture is placed in a long tube, and one part is locally stimulated, the reaction will proceed along the whole tube in the form of a wave. The mixture is an "isobolic" system, and obeys the "all or nothing" law. J. C. D.

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## Inorganic Chemistry.

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**Heat of Vaporisation of Hydrogen.** W. H. KEESOM (*Zeitsch. Sauerstoff Stickstoff Ind.*, 1919, ii, 83; from *Chem. Zentr.*, 1920, i, 147).—Dewar has determined the heat of vaporisation of hydrogen to be 123 *WE*; the author, however, gives the values 108·5—113·2, the greater probability of which is supported by theoretical considerations. H. W.

**Crystallography of Ice.** F. RINNE (*Ber. Verh. Sächs. Ges. Wiss., Math.-Nat. Kl.*, 1917, 69, 57—62; from *Jahrb. Min.*, 1919, Ref. 25—27).—The X-ray photograph of ice on the basal plane shows dihexagonal symmetry with  $a:c=1:1\cdot678$ , but does not decide whether the crystal is hemimorphic or not. Ice belongs to the magnesium type of the author's "isotypes" (*A.*, 1916, ii, 29), of which a tabulated list is given. L. J. S.

**Vapour Pressure of Solid Bromine.** TEÓFILO ISNARDI (*Ann. Physik*, 1920, [iv], 61, 264—272).—The vapour pressure of solid bromine has been determined at 0°, -10·9°, -15·5°, and -21·1° by two methods: (1) a manometric method, and (2) by allowing the vapour of bromine at measured temperature to fill a globe of known volume, condensing and weighing the liquid. The values obtained are considerably higher than those determined by Ramsay and Young (*T.*, 1886, 49, 453), except in the case of the value at 0°, which lies very near to that of Ramsay and Young. The following values are obtained: 0°, 65·83 mm.; -10·9°, 35·37 mm.; -15·5°, 24·95 mm.; and -21·1°, 15·75 mm. Extrapolation of the vapour-pressure curve to -41·3° gives values which agree very closely with those obtained by Cuthbertson by his optical method (*A.*, 1911, ii, 582). The triple point is calculated to lie at -7·3° and 46·4 mm. pressure. The vapour pressure of solid bromine is given by the formula  $\log p = a/T + b \log T + c$ , where the constants have the values  $a = -7109\cdot142$ ,  $b = -43\cdot33195$ , and  $c = 133\cdot46929$ . The heat of sublimation is calculated to 60·7 cal. per gram. J. F. S.

**Revision of the Atomic Weight of Fluorine.** E. MOLES and T. BATUCCAS (*J. Chim. Phys.*, 1919, 17, 537—588).—See this vol., i, 283.

**Mass of the Litre of Air and Gas Mixtures.** A. LEDUC (*Engineering*, 1919, 108, 569).—A résumé of the more important of the results published by Leduc (*Trav. Mem. Bureau Internat. Poids et Mesures*, 16). Two gases, A and B, both at pressure *P* and of equal volume, when mixed in double the volume have not the same pressure as before mixing, but a pressure  $P + \epsilon + \epsilon_1$ , where  $\epsilon$  and  $\epsilon_1$  depend on the nature of the gases. If the two gases are similar chemically,  $(\epsilon + \epsilon_1)$  is immeasurable, as, for example, is the

case with a mixture of carbon dioxide and nitrous oxide, but in the case of hydrogen and sulphur dioxide the mixture has a pressure 3 mm. greater than the pressure of the constituents. As regards the mixture of oxygen and nitrogen in the atmosphere,  $\epsilon$  may be disregarded. The density of air has been determined by direct weighing of air and from the weight of the constituent gases. Paris air has the following composition by volume (carbon dioxide and water vapour having been removed): oxygen, 0.2100; nitrogen, 0.7806; argon, 0.0094; neon,  $15 \times 10^{-6}$ ; helium,  $5 \times 10^{-6}$ ; hydrogen,  $1 \times 10^{-6}$ ; krypton,  $50 \times 10^{-9}$ , and xenon,  $6 \times 10^{-9}$ ; by weight: oxygen, 0.2321; nitrogen, 0.7549; argon, 0.0130; neon,  $8.4 \times 10^{-6}$ ; helium,  $0.7 \times 10^{-6}$ ; hydrogen,  $0.07 \times 10^{-6}$ ; krypton,  $140 \times 10^{-9}$ ; and xenon,  $30 \times 10^{-9}$ . The rare gases, with the exception of argon, only affect the density of air in the fifth decimal place. A litre of air at 0° and 760 mm. weighs 1.2928 grams when  $g=980.665$ ; under a pressure of 1 megabar, if  $g$  is 980.97 and the density of mercury is 13.5951, the weight is 1.2759 grams. Samples of air collected all over France and Algiers and at various altitudes show a weight percentage of oxygen varying between 23.05 and 23.25%. The oxygen percentage is lower in the north of France, and there is generally less oxygen close to the soil than at the height of foliage. J. F. S.

**Equilibrium in the System Ammonia-Ammonium Thiocyanate.** H. W. FOOTE and M. A. HUNTER (*J. Amer. Chem. Soc.*, 1920, **42**, 69—78).—With the object of finding an absorbent other than water for free ammonia, the system ammonia-ammonium thiocyanate has been investigated. The vapour pressure of ammonia-ammonium thiocyanate mixtures has been determined by passing ammonia at known pressure through a known weight of ammonium thiocyanate until no further increase in weight occurred; in this way the vapour pressure of ammonia is known. This was carried out at temperatures 0—40°. A further series of vapour-pressure measurements was made for saturated aqueous solutions of ammonia and ammonium thiocyanate at temperatures  $-78^\circ$  to  $+20^\circ$ , and the following values obtained:  $-78^\circ$ , 1 mm.;  $-65^\circ$ , 4 mm.;  $-50^\circ$ , 9 mm.;  $-34^\circ$ , 21 mm.;  $-23^\circ$ , 34 mm.;  $-20^\circ$ , 41 mm.;  $0^\circ$ , 107 mm.; and  $+20^\circ$ , 225 mm. The solubility of ammonium thiocyanate in ammonia has been determined at temperatures from  $0^\circ$  to  $50^\circ$ , and the following composition of saturated solutions is obtained:  $0^\circ$ , 23.3% ammonia, 76.7% thiocyanate;  $10^\circ$ , 22.65% ammonia, 77.35% thiocyanate;  $20^\circ$ , 21.6% ammonia, 78.4% thiocyanate;  $30^\circ$ , 20.15% ammonia, 79.85% thiocyanate;  $40^\circ$ , 18.4% ammonia, 81.6% thiocyanate;  $50^\circ$ , 16.65% ammonia, 83.35% thiocyanate. The specific conductivity of several solutions at  $0^\circ$  has been measured and the following values obtained: 75 mol. % ammonia,  $0.1979 \text{ ohms}^{-1}$ ; 68.9 mol. % ammonia,  $0.1640 \text{ ohms}^{-1}$ ; 63.3 mol. % ammonia,  $0.1395 \text{ ohms}^{-1}$ ; 59.7 mol. % ammonia,  $0.1246 \text{ ohms}^{-1}$ ; and 57.1 mol. % ammonia,  $0.1110 \text{ ohms}^{-1}$ . The vapour pressures found are much lower than Raoult's law requires. The practical application of ammonium thiocyanate as an absorbent

for ammonia has been considered, and it is shown that such an absorbent could be used in cases where it is necessary to eliminate water, and that a very large amount of the ammonia (98.1—99.6%) would be easily recoverable.  
J. F. S.

### Catalytic Oxidation of Ammonia to Nitric Acid.

B. NEUMANN and H. ROSE (*Zeitsch. angew. Chem.*, 1920, **33**, 41—44, 45—48, 51—55).—The authors have summarised the numerous processes and research in connexion with the catalytic oxidation of ammonia, and contribute some further results of investigations. Highest yields are obtained with platinum at 500° (96%), ferric oxide at 670° (90%), and iron-bismuth oxide at 600° (95%). The influence of the ammonia concentration, of the velocity of the gases, and of the temperature is discussed. Curves are given for the gas composition with various catalysts between 300° and 700°. Under definite conditions the oxidation will proceed continuously without external heat.  
W. J. W.

### Vapour Pressure of Arsenious Oxide in Sulphuric Acid Solutions.

F. SCHWERS (*J. Soc. Chem. Ind.*, 1920, **39**, 33—34r).—In the contact process for the manufacture of sulphuric acid, the sulphur dioxide is washed by bubbling through sulphuric acid. Experiments were made to determine to what extent arsenious acid is removed from the sulphuric acid by the sulphur dioxide, since any appreciable amount so carried forward would have a serious poisoning effect on the catalyst. In the experiments a measured volume of air was bubbled through sulphuric acid at 60° containing a known amount of arsenious oxide, and was then passed through a series of sodium hydroxide absorption tubes to collect any volatilised arsenic. The acid used contained, in two experiments, 0.015% and 0.001% of arsenious acid, and in each case small but appreciable amounts of arsenic were found in the absorption tubes, the amount carried forward being proportional to the amount present in the acid, and more than sufficient to have a poisoning effect on the catalyst.  
E. H. R.

### Atomic Weights of Boron and Fluorine.

EDGAR F. SMITH and WALTER K. VAN HAAGEN (*Carnegie Inst. Pub.*, 1918, **267**, 1—63).—Methyl alcohol obtained by the hydrolysis of methyl oxalate was used to prepare methyl borate, from which boric acid was produced by hydrolysis. The acid thus obtained and sodium carbonate gave borax, which was completely dehydrated by prolonged fusion. The anhydrous borax, by treatment with the appropriate acid and repeated evaporation with methyl alcohol, was converted into sodium chloride, sulphate, nitrate, and carbonate, from the weights of which the atomic weight of boron was calculated. The anhydrous borax was also indirectly converted into sodium fluoride through the formate, the direct conversion being impracticable.

The values obtained are 10.900 for boron and 19.005 for fluorine.

The boron value is 1% lower than the accepted value, which is erroneous owing chiefly to the retention of water by borax glass.

CHEMICAL ABSTRACTS.

**The Combustion of Wood Charcoal with Nitric Acid.**

FRIEDRICH C. G. MÜLLER (*Zeitsch. angew. Chem.*, 1920, **33**, 40).—Wood charcoal was heated in a current of nitric acid vapour and the resulting gases were collected and analysed. The gases had approximately the following composition:  $\text{CO}_2$ , 57.2%;  $\text{CO}$ , 13.3%;  $\text{H}_2$ , 4.6%;  $\text{N}_2$ , 24.9%. The high carbon monoxide content and the presence of free hydrogen are noteworthy. It was observed that a considerable quantity of ammonia was present in the condensate. The production of ammonia is difficult to account for, as the reaction temperature was at least  $1000^\circ$ .

E. H. R.

**Adiabatic Compression of Carbon Dioxide at High Temperatures.**

KURT NEUMANN (*Zeitsch. Ver. deut. Ing.*, 63, 1002—1007; from *Chem. Zentr.*, 1919, iii, 989).—The author has investigated the expansion of carbon dioxide which, enclosed in an insulated cylinder, had previously been heated to such a temperature that partial dissociation into carbon monoxide and oxygen had occurred (a phenomenon which is observed in internal combustion engines). During the expansion, combination of carbon monoxide and oxygen to carbon dioxide (after combustion) takes place, which has an important influence on the adiabatics. Expressions have been developed which permit the calculation of gaseous composition, pressure, and volume at a definite temperature.

H. W.

**Aqueous Solutions of Carbon Dioxide.** ROBERT STROHECKER (*Inaug.-Diss. Marburg*, 44 pp.; from *Jahrb. Min.*, 1919, *Ref.* 1).—Carbon dioxide solutions are important agents in geological processes. The slow neutralisation of such solutions by various bases was investigated, with the idea of gaining some idea as to their constitution. It appears that carbonic acid is not such a weak acid as is generally supposed, the dissociation constant being much higher than is usually stated. The acid constant was determined as  $k = 44 \cdot 10^{-5}$ ; it behaves, therefore, as an hydroxyformic acid.

L. J. S.

**Fall in Pressure, Density, and Heat of Vaporisation of Argon.**

A. CROMMELIN (*Zeitsch. Sauerstoff Stickstoff Ind.*, 1919, **11**, 81—83; from *Chem. Zentr.*, 1920, i, 147).—The latent heat of vaporisation of argon at  $-185.5^\circ$  is found to be  $69.4 \text{ WE}$ . Values for the fall in pressure and density at numerous temperatures are given in tabular form.

H. W.

**Surface Colours of Metals.** G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1919, 225—236; from *Chem. Zentr.*, 1920, i, 148).—Metals which yield surface colours become coated with a film of oxide, the rate of thickening of which with the time can be estimated by the alteration of the surface colours. Certain metals yield similar colours with iodine vapour at the ordinary tempera-

ture, and these are particularly suitable for the experimental investigation of the laws governing the rate of formation of the surface layer. The isothermal rate depends solely on the coefficient of diffusion of iodine into the layer of silver iodide covering the silver, and hence there is a parabolic dependence of thickness on time of action. The author's theory, which is confirmed by experiment, is based on the same fundamental ideas as Nernst's theory of solution. The actual chemical action occurs far more rapidly than the diffusion process, which, in the one case, leads to an attack of the reagent on the metal through a layer of constantly increasing thickness, whilst, in the other case, action occurs through a layer of constant thickness, since the deposit becomes detached. The quantitative relationships therefore depend on the different properties of the layers of reaction products. If crystals of iodine are placed in a desiccator over sulphuric acid, iodine vapour is observed which give surface colours with silver, copper, lead, and thallium; bismuth and antimony rapidly darken, and a fine, dark dust is deposited on their surfaces. Tin behaves similarly, but yields a yellow, incoherent layer. Small patches are formed within a few minutes on iron, cobalt, nickel, and manganese, and these, when removed from the desiccator, rapidly form droplets since the iodides are hygroscopic. Zinc and cadmium are more regularly, but much more slowly, attacked; with chromium, action is doubtful. With metals which give surface colours, the rate of increase of the layer which causes the coloration can be determined if care is taken to keep the concentration of iodine vapour constant. For this purpose air is drawn through a definite iodine solution, and the surface colour is compared at definite intervals with a table which gives the relationship between surface colour and thickness of film. A strip of silver shows three different types of behaviour towards iodine according to whether it has been rolled and cleaned, has been melted and thus covered with large crystallites, or has been left unworked and thus covered with multitudinous, small, dendritic crystals. The surface colorations on copper are similar to those on silver which has been similarly treated. Since, however, the index of refraction of copper iodide has not been determined, the thickness corresponding with the colours of the corresponding layers of air cannot be calculated to actual thicknesses of iodide film. In many regions of temperature, the rate of increase of the superficial layer is independent of the temperature; this is true in the case of steel, for which the author gives calculations based on Löwenherz's experiments. H. W.

**Segregation Dispersoids in Anisotropic Media.** WILHELM EITEL (*Centr. Min.*, 1919, 173—183).—When homogeneous mixtures of sodium and potassium chlorides are cooled rapidly from a high temperature, metastable, homogeneous mixed crystals can be obtained which, however, when maintained for some time at a suitable temperature, decompose into the constituent salts, the crystals becoming opaque. This phenomenon has been investigated by the

ultramicroscopic method used by Lorenz and Eitel for the examination of metallic fogs in crystals of the corresponding chlorides (A., 1915, ii, 260, 261). A complete series of mixtures of the two salts was examined, and it was shown that the segregation of the mixture can be optically demonstrated under the ultramicroscope through the gradual formation of a fog or fine dispersoid phase at a temperature of about  $250^{\circ}$ . A number of photographs are reproduced.

E. H. R.

### **Solidification Points of Mixtures of Metallic Chlorides.**

FRED. C. A. H. LANTSBERY and R. A. PAGE (*J. Soc. Chem. Ind.*, 1920, **39**, 37—41 $\pi$ ).—The authors have determined the freezing-point curves of the three binary mixtures and one ternary mixture comprised in the system sodium chloride—potassium chloride—calcium chloride by the cooling method, that is, plotting the cooling curve of a mixture of known composition and noting the arrest point. In the sodium chloride—potassium chloride series the components form a continuous series of solid solutions; the lowest melting mixture contains 55% KCl and 45% NaCl, and solidifies at  $650^{\circ}$ . The curve for the sodium chloride—calcium chloride series shows a very sharp minimum at 72.5%  $\text{CaCl}_2$  and 27.5% NaCl; the corresponding freezing point is  $505^{\circ}$ . The potassium chloride—calcium chloride series is more complicated. The curve shows two distinct eutectic points and a maximum between them at about 70%  $\text{CaCl}_2$ . The maximum corresponds with a freezing point of  $725^{\circ}$  and represents the formation of a compound,  $2\text{KCl}, 3\text{CaCl}_2$ . The eutectic between the compound and  $\text{CaCl}_2$  freezes at  $608^{\circ}$  and contains 17.5% KCl, whilst that between the compound and KCl freezes at  $590^{\circ}$  and contains 60% KCl. The results do not confirm the work of Menge (A., 1911, ii, 982), who reported the formation of a compound,  $4\text{NaCl}, \text{CaCl}_2$ , in the sodium chloride—calcium chloride series. Freezing-point determinations were made on a series of forty-one ternary mixtures, and the results are plotted on a triangular diagram in which the isothermal lines are shown. There are two ternary eutectics, one containing 70%  $\text{CaCl}_2$ , 25% NaCl, and 5% KCl, freezing at  $495^{\circ}$ , the lowest in the series, the other containing 30%  $\text{CaCl}_2$ , 20% NaCl, and 50% KCl, freezing at  $530^{\circ}$ .

E. H. R.

**Additive Products of Sulphur Dioxide and Alkali Iodides (Alkali iodide Sulphones).** FRITZ EPHRAIM (*Ber.*, 1920, **53**, [B], 118).—The alkali iodides absorb varying proportions of sulphur dioxide (A., 1916, ii, 614), whereas Forcrand and Taboury have recently stated that sulphones of the type  $\text{MI}, 3\text{SO}_2$  are produced (A., 1919, ii, 341).

J. C. W.

**The Dissociation of Ammonium Carbamate.** C. MATIGNON and M. FRÉJACQUES (*Compt. rend.*, 1920, **170**, 462—464).—The values obtained by Naumann (this Journ., 1871, 1195) for the dis-

sociation pressures of ammonium carbamate over the temperature range  $-15^{\circ}$  to  $+60^{\circ}$  may be expressed by two equations:

$$\log p = -3.635/T - 7.045 \log T + 28.692$$

and

$$\log p = -4.821/T - 15.4 \log T + 53.3586.$$

Measurements made at  $81^{\circ}$  and  $93^{\circ}$ , where the pressures are several atmospheres, confirm the accuracy of these equations. Calculations made by means of these equations give the heat of dissociation of ammonium carbamate, at constant pressure, as  $-39.0$  cal., which is in close agreement with the value previously found by experiment (compare Matignon, A., 1908, ii, 465). W. G.

### Growth Phenomena of Copper, Silver, and Gold.

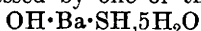
A. BEUTELL (*Centr. Min.*, 1919, 14—28).—When natural or artificial silver sulphide is heated in an evacuated sealed tube for several days at a temperature of  $350$ — $600^{\circ}$  a certain amount of decomposition takes place. The small amount of silver formed seems to wander through the silver sulphide, appearing at the cooler end of the tube in the form of hair silver. A number of experiments which were made showed that neither silver foil nor hair silver is attacked by sulphur vapour in a vacuum at  $450^{\circ}$ ; the metal remained bright after forty-eight hours. Silver foil heated alone in a vacuum for a long period at  $450$ — $585^{\circ}$  showed no trace of the growth of hair silver, but when silver foil and silver sulphide were heated together at  $450^{\circ}$  remarkable growths were obtained in a comparatively short time. To obtain these growths it is necessary for the silver and the silver sulphide to be actually in contact. Similar growths of copper were obtained by heating together copper and cuprous sulphide, but the process was much slower. When silver selenide or telluride was used in place of the sulphide, similar growths of silver were obtained, and hair copper was obtained to a certain extent with copper selenide and telluride. With gold, the best results were obtained when gold telluride containing silver was heated with silver foil. After seven days' heating at  $500^{\circ}$ , growths of "moss" gold containing silver had appeared at the cooler end of the tube. E. H. R.

### Action of Water on Strontium Sulphide. E. TERRES and

K. BRÜCKNER (*Zeitsch. Elektrochem.*, 1920, 26, 25—32).—The action of water on strontium sulphide has been investigated. It is shown that the reaction in this case differs materially from the reaction in the case of barium sulphide (see following abstract). In the present case the reaction takes place between two molecules of water and two molecules of sulphide with the formation of equimolecular quantities of strontium hydroxide and strontium hydrosulphide:  $2\text{SrS} + 2\text{H}_2\text{O} = \text{Sr}(\text{SH})_2 + \text{Sr}(\text{OH})_2$ . The hydroxide and hydrosulphide, in consequence of their widely differing solubility, may be completely separated by crystallisation. When strontium sulphide is extracted with hot water and the clear filtrate cooled, pure strontium hydroxide crystallises. The solubility of strontium

hydrosulphide has been determined at temperatures 0—100°, and the following values obtained in grams of the anhydrous compound per 100 grams of water: 0°, 27.5; 20°, 29.7; 40°, 31.6; 60°, 33.2; 80°, 35.6; 100°, 37.8. The solubility of strontium hydroxide and strontium hydrosulphide in the same solution has been determined over the range 0—100°, and it is shown that no mixed compound is formed and that the hydroxide and hydrosulphide are in equilibrium with one another at all temperatures. Hence strontium hydroxide may be prepared by direct crystallisation of the solution obtained by the action of water on strontium sulphide. J. F. S.

**Action of Water on Barium Sulphide.** E. TERRES and K. BRÜCKNER (*Zeitsch. Elektrochem.*, 1920, **26**, 1—24).—The conditions influencing the formation of barium hydroxide from barium sulphide are experimentally investigated. A long list of patents and investigations is given with short critical remarks. A number of processes are repeated which are based on the action of water on barium sulphide and in which the crystalline product is worked up to barium hydroxide either by crystallisation or by treatment with metallic oxides. The results confirm in many cases the published accounts. The concentration of the solution and the composition of the residue, obtained by extracting barium sulphide with water at various temperatures, are investigated. The content of the solution of barium hydroxide and barium hydrosulphide increases rapidly with increasing temperature. The solid residue consists to the extent of  $\frac{1}{3}$ — $\frac{1}{4}$  of barium oxide. The solutions contain equal molecular quantities of hydroxide and hydrosulphide, so that it would appear as though in the presence of one another these substances had the same solubility in water. The action of barium hydroxide solution on barium sulphide shows, however, that the solution is not saturated with barium hydroxide. Hence it would seem that the solution is saturated with an intermediate compound, either an hydroxyhydrosulphide or a double compound of barium hydroxide and barium hydrosulphide, but it is not saturated with the components of this double compound. The solubility of barium hydrosulphide is determined from -15° to 100°. It is shown that the intermediate compound is formed when barium hydroxide and barium hydrosulphide are mixed in definite proportions, and that the maximum quantity of the compound is precipitated when twenty-seven molecules of the hydrosulphide are mixed with one molecule of the hydroxide; also the greater the excess of hydrosulphide the purer the precipitated double compound. The double compound may be expressed by one of the formulæ



or  $\text{Ba}(\text{OH})_2, \text{Ba}(\text{SH})_2, 10\text{H}_2\text{O}$ . Experiments on the solubility of the intermediate compound show that the solution contains the components in very different proportions to the solid substance, that is, the undissolved residue contains an excess of hydroxide. The intermediate compound is shown to possess a considerable stability except towards oxidising agents, and there is no considerable decom-



position by water either with or without pressure or even by alkalis. The compound in relation to the hydrosulphide possesses a very small hydrogen sulphide pressure. For these and other reasons the author allots the formula  $\text{OH}\cdot\text{Ba}\cdot\text{SH}\cdot 5\text{H}_2\text{O}$  to this compound. The solubility of barium hydroxide and barium hydrosulphide simultaneously has been determined from the cryohydric point to  $100^\circ$ . At all temperatures the region of existence of the double compound lies between those of barium hydroxide and barium hydrosulphide. The two simple compounds, therefore, can never exist together in the same solution, but must combine to form the intermediate product. It also follows that pure barium hydroxide can never be crystallised from the solution obtained by the action of water on barium sulphide. J. F. S.

**Solubility of Zinc in Cyanide Solutions.** H. A. WHITE (*J. Chem. Met. Min. Soc. S. Africa*, 1919, **20**, 97—101).—From the results of an investigation made to determine the effect of various practical conditions on the solution of zinc during the precipitation of gold from cyanide solutions, it is concluded that close regulation of cyanide strength, alkalinity, and aeration of the auricyanide solution is necessary if the consumption of zinc is to be kept within reasonable limits. The ideal of a zinc consumption corresponding even approximately with the amount of gold precipitated appears unlikely to be attained. [For further details, see *J. Soc. Chem. Ind.*, 1920, April.] W. E. F. P.

**Attempt to Determine if Common Lead could be Separated into Isotopes by Centrifuging in the Liquid State.** J. JOLY and J. H. J. POOLE (*Phil. Mag.*, 1920, [vi], **39**, 372—375).—Molten lead has been centrifuged at a rate of 9000 revolutions per minute in electrically heated steel tubes for periods of one hour. The top and bottom layers were then withdrawn and cast into pellets, and the density determined. Although small differences between the density of the two layers are observed, they lie inside the experimental error, so that the experiments furnish no evidence that a separation of the isotopes has been effected.

J. F. S.

**Effect of Centrifuging certain Alloys while in the Liquid State.** J. JOLY and J. H. J. POOLE (*Phil. Mag.*, 1920, [vi], **39**, 376).—Using the method described above (see preceding abstract), it is found that silver-lead alloys could not be appreciably separated by centrifuging, but lead-tin alloys could be to some extent separated. Thus with an alloy containing 82% of lead and 18% of tin the top layer was 1.8% lighter than the bottom layer after centrifuging.

J. F. S.

**The Action of Water on Lead.** J. F. LIVERSEEGE and A. W. KNAPP (*J. Soc. Chem. Ind.*, 1920, **39**, 27—33T).—The experiments here recorded on the action of water on lead were made with the waters collected in the Caban reservoir, Elan Valley, Wales, for

the use of Birmingham. These waters have a slight alkalinity, due to hydrogen carbonates, etc., equal to about 0.3 part  $\text{CaCO}_3$  per 100,000. The action of such waters, and generally of waters the alkalinity of which does not exceed 1.5, is erosive. The whole surface of the lead is attacked and a flocculent precipitate forms, which, becoming detached, leaves the surface of the lead bright but mottled. When the alkalinity is increased to 1.5—2.5 the action becomes corrosive, and a loosely-held, white, opaque crust forms here and there on the surface. With still greater alkalinity the lead almost invariably becomes covered with a dull white film, which appears to act as a protective coating. The erosion tests were made by the method of Houston, in which a clean strip of lead of standard size is immersed in the water in a test-tube, air having free access. The amount of lead eroded is determined colorimetrically as sulphide. It proved possible to carry out the test in one day. It was found that such variations as occurred naturally in the amount of oxygen present in the water had no appreciable effect on the erosion. Variations in the amount of water used did not affect the amount of erosion, but the greater the depth of immersion of the lead the smaller was the velocity of attack. Exposure to glass lowered the erosive ability of the water. Erosion readily occurred in waters free from carbon dioxide, and small variations in the carbon dioxide content had no appreciable effect. The presence, however, of from 1 to 2% of carbon dioxide by volume caused a sudden change from erosion to "plumbo-solvency," that is, the lead precipitate no longer appears but soluble lead hydrogen carbonate is formed. Carbon dioxide dissolves lead more rapidly in presence of oxygen than alone. It is concluded that, given oxygen present, the principal factor in determining both amount and kind of erosion is the alkalinity of the water. The addition of small quantities of calcium hydroxide, carbonate, or hydrogen carbonate or of potassium permanganate decreases erosion, but calcium hydrogen carbonate is most effective; erosion occurs in absence of bacteria. It was observed that the bacteria in the water are not all destroyed by exposure to lead for six hours.

E. H. R.

**The Alloys of Copper, Zinc, and Nickel.** LÉON GUILLET (*Compt. rend.*, 1920, 170, 460—462).—Brasses containing nickel, in which the copper content falls to 40% and even less and the nickel content rises to 15%, are of particular interest because of their mechanical properties. Their breaking strain varies from 45 to 75 kilos./mm.<sup>2</sup> with elongations of 45—18%. They are readily malleable at high temperatures, and in colour and resistance to oxidation they are comparable to German silver. W. G.

**Compressibility of Indium.** THEODORE W. RICHARDS and JITSUSABURO SAMESHIMA (*J. Amer. Chem. Soc.*, 1920, 46, 49—54).—The compressibility of indium has been determined over the pressure range 100—500 megabars. The measurements were made

at 25°. At this temperature indium has a density 7.318. The measurements were carried out by the usual method, but instead of a steel piezometer, as previously used, a small glass one was made use of in the present work. It is found that the compressibility of indium over the range examined is 0.0000027, or about two-thirds that of mercury.

J. F. S.

**The Limits of the Combining Power of Silicon with certain Metals of the Iron Group.** A. SANFOURCHE (*Rev. Mét.*, 1919, **16**, 239—245; from *Chem. Zentr.*, 1920, i, 149—150).—The uncertainties in the literature concerning the combining power of silicon with members of the iron group are frequently to be ascribed to faulty methods of analysis consisting in the treatment of the alloy with alkaline reagents to effect removal of the excess of silicon and isolation of the alloy richest in silicon from the residue. Actually, the persilicated compounds are frequently attacked in the circumstances, whilst removal of the free silicon enclosed in the alloy is frequently incomplete. In addition, the combining power of silicon with iron and related substances is not a constant quantity, but depends on various factors, notably on the excess of free silicon. In ferrosilicons, the lower limit of combining power lies at 55.55% Si, corresponding with the formula  $\text{Fe}_2\text{Si}_5$ , the upper limit at 60% Si corresponding with  $\text{FeSi}_3$ . With manganese-silicon alloys the limit lies between 46.70 and 50.11% Si; the upper value is here obtained with 8% of free silicon, whilst for iron, in similar circumstances, a 2% excess of silicon suffices. The higher limit approximates to the formula  $\text{MnSi}_2$ , so that this compound may be regarded as having the highest possible silicon content; the lower limit does not correspond with a definite compound, whilst the substance  $\text{MnSi}_2$  appears to require the presence of a sufficient excess of silicon to prevent its dissociation with liberation of this element. The influence of silicon is also very noticeable with cobalt silicon alloys; as it increases from 0% to 6% the combining power increases from 50% to about 53%. Neither limit corresponds with a definite chemical compound; the simple formulae to which they most closely approximate are  $\text{CoSi}_2$  (48.7% Si) and  $\text{Co}_3\text{Si}_5$  (54.26% Si). With nickel-silicon alloys the limits of combining power are most widely separated (39—45%); in this case also a definite compound is not indicated. The upper limit is only attained in the presence of at least a 10% excess of free silicon.

The method of analysis consists in the estimation of total silicon by treatment with alkali carbonate and of uncombined silicon by removal of the combined element as silicon tetrafluoride by treatment with pure hydrofluoric acid. Combined silicon is estimated by difference.

The author is led to the conclusion that compounds of the iron group rich in silicon tend to dissociate partly into free silicon and a more or less well-defined compound of silicon and the metal:  $\text{M}_x\text{Si}_y \rightleftharpoons \text{M}_x\text{Si}_{y-z} + \text{Si}_z$ . Stabilisation occurs in the presence of a sufficient excess of silicon, but, if this is present in quantity only

sufficient to form the compound, a certain amount of it passes into the free condition (in solution) and so depresses the combining power. H. W.

**Form of Ultra-microscopic Platinum Particle.** RICHARD GANS and RICARDO CALATRONI (*Ann. Physik*, 1920, [iv], **61**, 465—470).—Using platinum sols prepared both by the Bredig process and by reduction of chloroplatinic acid with hydrazine hydrate in the presence of the sodium salt of protalbic acid as protecting colloid, the authors have measured the absorption for the four helium lines  $\lambda\lambda$  6678, 5877, 5010, and 4472 Å. units. To ensure uniformity of the particles and to remove aggregates, the solutions were filtered through collodion ultra-filters which contained 0.5—1.0% of acetic acid. The results show that as in the case of silver and gold amicros (A., 1912, ii, 508; 1915, ii, 390), the platinum amicros are spherical in form (see also Diesselhorst and Freundlich, *Physikal. Zeitsch.*, 1916, **17**, 117). J. F. S.

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### Mineralogical Chemistry.

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**The Composition of Coal. The Behaviour of the Constituents of Banded Bituminous Coal on Coking.** RUDOLF LESSING (T., 1920, 117, 247—256).

**The Composition of Coal. The Mineral Constituents of Banded Bituminous Coal.** RUDOLF LESSING (T., 1920, 117, 256—265).

**Villamaninite, a New Mineral.** W. R. SCHOELLER and A. R. POWELL (*Min. Mag.*, 1920, 19, 14—18).—As black, crystalline grains and small nodules, this occurs disseminated plentifully in a matrix of white, crystalline dolomite, which contains also some iron-pyrites, copper-pyrites, and quartz. It is from the Carmenes mines, near Villamanin, prov. Leon, Spain. Material isolated by dissolving away the dolomite matrix is seen to consist of small groups of rough crystals which show the forms of the cube and octahedron. The cube faces show a peculiar rounding, and it is these faces that form the bright convex and concave surfaces of the nodules. These nodules, never more than sectors of spheres, are due to the subparallel aggregation of crystals. The colour is iron-black with dull metallic lustre, and the streak is sooty-black;  $H=4\frac{1}{2}$ . The mineral is soluble in nitric acid, leaving a globule of sulphur. Heated in a bulb-tube it gives a sublimate of sulphur and selenium, and it burns in the air with a blue flame. Analysis I is of hand-picked, nodular material; II, of acid-cleaned nodular;

III, acid-cleaned crystalline; and IV, of acid-cleaned unsorted. Also traces of arsenic, bismuth, lead, and zinc:

	S.	Se.	Cu.	Ni.	Co.	Fe.	SiO <sub>2</sub> .	Total.	Sp. gr.
I.	49.00	1.54	17.65	18.19	7.45	4.39	0.88	99.10	—
II.	49.13	1.44	18.51	18.24	7.24	4.17	0.34	99.07	4.433
III.	49.63	0.88	22.13	15.94	6.30	5.11	0.22	100.21	4.523
IV.	47.27	0.88	19.48	15.53	6.79	6.00	3.80	99.75	—

The atomic ratios  $(S + Se) : (Cu + Ni + Co + Fe) = 1.953, 1.936,$  and  $1.904$  for analyses I, II, and III respectively, approximating to the disulphide formula,  $(Cu, Ni, Co, Fe)(S, Se)_2$ . The presence of copper, nickel, and cobalt in a disulphide is discussed. L. J. S.

**The Structure and Symmetry of Anatase, Rutile, Zircon, and Xenotime.** A. JOHNSEN (*Centr. Min.*, 1919, 97—105).—Crystals of these minerals have been investigated by the X-ray method by Vegard (A., 1916, ii, 405, 593), who came to definite conclusions regarding their inner structure. Vegard's structures have been critically examined by the author, who finds that, whilst those of anatase, rutile, and xenotime are tetragonal holohedral, that of zircon must belong either to the hemimorphous hemihedral or to the hemimorphous tetartohedral class. Experiments on the pyro- and piezo-electric properties of crystals of zircon are desirable to test the point. E. H. R.

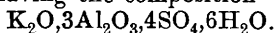
**Dolomite from Leogang, Salzburg.** O. GROSSPIETSCH (*Tsch. Min. Mitt.*, 1917, **34**, 68—70; from *Jahrb. Min.*, 1919, Ref. 274).—Blackish-grey crystals with the form of acute rhombohedra gave:

(CO <sub>2</sub> + trace of S).	FeO.	CaO.	MgO.	Total.	Sp. gr.
47.53	1.63	29.66	21.18	100.00	2.889

The sulphur is due to admixed pyrites.

L. J. S.

**A Singly Refracting Potassium Aluminium Sulphate of the Alunite Group.** E. RAMANN and A. SPENGEL (*Centr. Min.*, 1919, 35—37).—Among the decomposition products of the rocks of the Solfatara di Puzzuoli, Naples, has been found a potassium aluminium sulphate having the composition



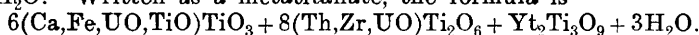
It seems to have been formed by the action of sulphuric acid on the volcanic rock, and occurs, mixed with sulphur and silica, in the form of very fine particles, 0.001 to 0.002 mm. in diameter. It is singly refracting, but whether it is amorphous or belongs to the regular system it is difficult to say on account of the small size and rounded form of the particles. E. H. R.

**Brannerite, a New Uranium Mineral.** FRANK L. HESS and ROGER C. WELLS (*J. Franklin Inst.*, 1920, **189**, 225—237).—This is found as grains and rough prisms (tetragonal or orthorhombic?) in gold placers in Stanley Basin, central Idaho. The fragments

have a thin, brownish-yellow crust, but inside the material is brilliant black with conchoidal fracture. Opaque; streak, dark greenish-brown; H, 4½. Thin splinters transmit yellowish-green light, and are optically isotropic;  $n_{Li} = 2.26$ ,  $n_{Na} = 2.30 \pm 0.02$ ; D 4.5—5.43; fragments of higher density are more strongly radioactive. The mineral is slowly decomposed by concentrated sulphuric acid and by hydrofluoric and sulphuric acids. For the analysis it was fused with hydrogen sodium sulphate. Details are given of the method of analysis; titanium and uranium were separated by hydrolysis. In determining the state of oxidation of the uranium, the iron was assumed to be all ferrous, and this introduces a difficulty in deducing a formula. Other determinations of iron gave on unselected material  $Fe_2O_3$  3.7%, and on the best selected material  $Fe_2O_3$  3.0 or  $FeO$  2.7%. The least radioactive material contained  $TiO_2$  35.0%. Analysis by R. C. Wells (also traces  $Fe_2O_3$ ,  $Al_2O_3$ ,  $P_2O_5$ ):

SiO <sub>2</sub> .	TiO <sub>2</sub> .	FeO.	CaO.	UO <sub>2</sub> .	UO <sub>3</sub> .	ThO <sub>2</sub> .	Ce <sub>2</sub> O <sub>3</sub> .	Yt <sub>2</sub> O <sub>3</sub> , etc
0.6	39.0	2.9	2.9	10.3	33.5	4.1	nil	3.9
ZrO <sub>2</sub> .	PbO.	BaO.	SrO.	H <sub>2</sub> O.	CO <sub>2</sub> .	Total.	Sp.gr.	
0.2	0.2	0.3	0.1	2.0	0.2	100.2	5.42	

This analysis gives the ratios 9RO, Yt<sub>2</sub>O<sub>3</sub>, 5RO<sub>2</sub>, 11UO<sub>3</sub>, 46TiO<sub>2</sub>, 10H<sub>2</sub>O. Written as a metatitanate, the formula is



Many analyses of complex uranium minerals are tabulated. Brannerite contains more uranium than any, with the exception of pitchblende. It appears to be nearest delorenzite (A., 1908, ii, 604), but contains less titanium and rare earths.

L. J. S.

**Crystal Structures of Wulfenite and Scheelite.** ROSCOE G. DICKINSON (*J. Amer. Chem. Soc.*, 1920, **42**, 85—93).—The X-ray spectra of several planes of wulfenite ( $PbMoO_4$ ) and scheelite ( $CaWO_4$ ) have been measured and tabulated. For wulfenite the following values of  $n$  and  $\sin \frac{1}{2}\phi_n$  are obtained, together with the intensities  $I$ , plane 101:  $n=1$ ,  $\sin \frac{1}{2}\phi_n = 0.0915$ ,  $I=100$ ;  $n=2$ ,  $\sin \frac{1}{2}\phi_n = 0.1828$ ,  $I=66$ ;  $n=3$ ,  $\sin \frac{1}{2}\phi_n = 0.2754$ ,  $I=30$ ;  $n=4$ ,  $\sin \frac{1}{2}\phi_n = 0.3657$ ,  $I=13$ ; and  $n=5$ ,  $\sin \frac{1}{2}\phi_n = 0.4553$ ,  $I=5$ . Measurements are also made for the planes 100, 110, 001, 111, and 102. In the case of scheelite two sets of values were obtained, using different specimens, plane 101:  $n=1$ ,  $\sin \frac{1}{2}\phi_n = 0.0950$ ,  $I=100$ ;  $n=2$ ,  $\sin \frac{1}{2}\phi_n = 0.1905$ ,  $I=59$ ;  $n=3$ ,  $\sin \frac{1}{2}\phi_n = 0.2860$ ,  $I=18$ ;  $n=4$ ,  $\sin \frac{1}{2}\phi_n = 0.3805$ ,  $I=8$ . The planes 100, 110, 001, and 111 were also measured. It is shown that the face-centred lattice, with atoms so located as to form a diamond arrangement, accounts in each case for the relative spacings of different planes, and for the density of the crystals. The arrangement of the heavier atoms relative to one another has been determined by a qualitative consideration of the relative intensities. The difficulties in the location of the oxygen atoms are discussed.

J. F. S.

[**Composition**] of **Davidite**. W. T. COOKE (*Trans. R. Soc. South Australia*, 1916, **40**, 267).—Material from Radium Hill, near Olary, South Australia, gave:

TiO <sub>2</sub> .	FeO.	Fe <sub>2</sub> O <sub>3</sub> .	Ce <sub>2</sub> O <sub>3</sub> , etc.	U <sub>3</sub> O <sub>8</sub> .	CaO.	MgO.	PbO.	H <sub>2</sub> O.	Total.
54.3	16.0	13.0	8.3	4.6	1.5	0.6	1.1	1.5	100.9

The cerium earths include much Ce, little Th, also La, Di, Er, Yt. Also some V<sub>2</sub>O<sub>5</sub> and Cr<sub>2</sub>O<sub>3</sub>, included with the uranium oxide, trace of copper, and scandium detected spectroscopically. At a red-heat 100 grams of the mineral yielded about 15 c.c. of fairly pure helium. D. MAWSON in a preceding paper (*loc. cit.*, 262—266) describes the mode of occurrence of the mineral, and states it to be homogeneous (compare A., 1910, ii, 309). L. J. S.

**Siliceous Sinter from Lustleigh, Devon.** A. B. EDGE (*Min. Mag.*, 1920, **19**, 10—13).—Lodes traversing granite and containing a soft and powdery, micaceous hæmatite are worked at the Plumley mine. In one lode, however, this mineral is present as larger scales, and it is cemented into a hard, stony mass by siliceous sinter, which contains also crystals of fluor-apatite, tourmaline, and quartz. The sinter is hard and compact, but very fragile. It ranges in colour from almost pure white to blood-red, with rippled and folded bands of colouring. Analysis of pale red material gave (also CaO, P<sub>2</sub>O<sub>5</sub>, traces):

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O at 105°.	H <sub>2</sub> O >105°.	Total.	Sp. gr.
69.76	2.68	5.38	0.36	0.76	18.62	2.38	99.94	1.73

The origin of the material is discussed; it was evidently deposited as a silica jelly. L. J. S.

**Hemimorphite on Fossil Bones from Broken Hill, Rhodesia.** H. BUTTGENBACH (*Ann. Soc. Géol. Belgique*, 1919, **42**, *Congo Annexe*, 5—14).—Limb bones of mammals from the cave at Broken Hill mine (A., 1908, ii, 397) show (1) compact tissue consisting of calcium phosphate and carbonate with a trace of fluorine, but no chlorine or zinc; (2) a glistening, crystalline crust (anal. I) of hemimorphite coating the compact tissue externally and internally; (3) a spongy aggregate (anal. II) of minute crystals of willemite, smithsonite, hemimorphite, hopeite, parahopeite, and tarbuttite occupying the central cavity.

	ZnO.	Fe <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> .	CaO.	SiO <sub>2</sub> .	P <sub>2</sub> O <sub>5</sub> .	Ign.	Total.
I.	63.10	1.22	1.68	22.88	1.38	9.30	99.56
II.	45.50	0.82	15.24	15.00	12.75	10.22	99.53

L. J. S.

[**Halloysite from Worms Heath, Croydon, Surrey.**] GEORGE MACDONALD DAVIES (*Quart. J. Geol. Soc.*, 1920, **75** [for 1919], 22—28).—A petrographical description is given of the



materials (clay, sand, and pebbles) filling large, vertical pipes in the chalk at this locality. A white, clay-like material found in the sand in these pipes, and previously referred to allophane, is proved by the following analysis, by A. B. EDGE, to be halloysite. Formula,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} + \text{Aq.}$  Also traces of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ . D 2.44;  $n$  near 1.552. (After ignition, D 2.46 or 2.47;  $n$  about 1.542.)

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	CaO.	$\text{H}_2\text{O}$ (at 100°)	$\text{H}_2\text{O}$ (100–250°).	$\text{H}_2\text{O}$ (ign.).	$\text{CO}_2$ .	Total.
41.88	36.26	0.30	0.23	7.71	0.85	13.06	0.17	100.46

L. J. S.

**The Scapolites.** NILS SUNDIUS (*Bull. Geol. Inst. Univ. Upsala*, 1918, 16, 96–106; from *Jahrb. Min.*, 1919, *Ref.* 140–142).—Supplements previous work (A., 1919, ii, 163). An analysis by Mauzelius (1917) of scapolite from gabbro at Nautanen, Lapland, D 2.698, is calculated as marialite 29.17, sulphate-marialite 9.38, carbonate-meionite 61.46%, and the mineral has the refractive indices  $\omega$  1.575,  $\epsilon$  1.552. The composition of carbonate-marialite is now written as  $\text{NaHCO}_3 \cdot 3\text{NaAlSi}_3\text{O}_8$ , and of sulphate-marialite as  $\text{NaHSO}_4 \cdot 3\text{NaAlSi}_3\text{O}_8$ . Scapolite from lime-silica gneiss in the Gula valley, Trondjem, Norway, gave analysis I ( $\text{Na}_2\text{O}$ ,  $\text{H}_2\text{O}$  not determined), corresponding with marialite 6, carbonate-marialite 31, carbonate-meionite 63; it has  $\omega$  1.585,  $\epsilon$  1.551.

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	CaO.	MgO.	Cl.	$\text{SO}_3$ .	$\text{CO}_2$ .	Total.
I. 48.87	27.55	0.62	15.65	0.18	0.24	—	4.16	97.27

In scapolite from the Laacher See, a redetermination of carbon dioxide in the original material analysed by Brauns (*anal. I*, A., 1917, ii, 325) gave 3.23% (as against 0.65%), corresponding with marialite 13, sulphate-marialite 10, sulphate-meionite 9, carbonate-meionite 68%; this has  $\omega_{\text{Na}}$  1.5901,  $\epsilon_{\text{Na}}$  1.5600. Another, also described by Brauns in 1914, contains  $\text{CO}_2$  3.52% (rather than 0.26%), corresponding with marialite 6, carbonate-marialite 31, carbonate-meionite 63, and has  $\omega - \epsilon = 0.0284$ . In their optical constants, these sulphate-rich scapolites do not differ from the carbonate-scapolites, and they fall into the same series.

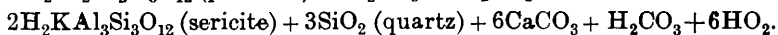
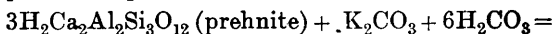
L. J. S.

**Prehnite from the Tatra Mountains.** W. PAWLICA (*Bull. Acad. Sci. Cracow*, [A], 1916, 54–59; from *Jahrb. Min.*, 1919, *Ref.* 275–276).—Massive, white prehnite with associated epidote, albite, and calcite fills veinlets in oligoclase-biotite-granite on the Mengesdorf peak. In the vicinity of these veins the granite is much decomposed, suggesting that the minerals were deposited by hydrothermal processes. Cavities in the massive mineral are lined with

small crystals of prehnite. The mean of two analyses is (also traces of MnO, MgO, K<sub>2</sub>O, Na<sub>2</sub>O):

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	H <sub>2</sub> O at 110°.	H <sub>2</sub> O > 110°.	Total.	Sp.gr.
43.89	23.85	1.56	0.28	25.83	0.23	4.52	100.16	2.904

The prehnite is in places altered to a powdery aggregate of sericite scales and quartz grains, being sometimes represented as pseudomorphs. This alteration is expressed as follows:

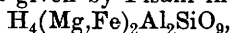


L. J. S.

**A New Description of Amesite.** EARL V. SHANNON (*Amer. J. Sci.*, 1920, [iv], **49**, 96—98).—A specimen from the disused emery mine at Chester, Massachusetts, shows hexagonal plates 1 cm. across of pale bluish-green amesite, with associated diaspore, magnetite, and rutile. The basal cleavage is not so perfect as in most other chlorites; H 2½, D 2.77. The crystals are optically positive and biaxial, but with very small axial angle;  $\alpha = \beta = 1.597$ ,  $\gamma = 1.612$ . Before the blowpipe, the mineral swells and exfoliates slightly, becoming silvery brownish-white in colour. It is partly decomposed by boiling sulphuric, nitric, or hydrochloric acid, with separation of flocculent silica. Most of the water is lost at only a dull red heat. Analysis:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	MnO.	H <sub>2</sub> O > 110°.	H <sub>2</sub> O > 110°.	Total.
20.95	35.21	8.28	0.58	22.88	trace	0.23	13.02	101.15

agrees with the formula given by Pisani in 1876, namely,



except for the ratio MgO:FeO, which is here = 5:1. This formula was adopted by Tschermak in 1890 for a fundamental end-member of the chlorite group.

L. J. S.

**Optical Characters of the Olivine Group.** H. MAGNUSSON (*Geol. För. Förh.*, 1918, **40**, 601—626; from *Jahrb. Min.*, 1919, *Ref.* 277—279).—Previous attempts at the correlation of the optical constants and the chemical composition of the members of the olivine group (A., 1911, ii, 616) have been confined to the series Mg<sub>2</sub>SiO<sub>4</sub>—Fe<sub>2</sub>SiO<sub>4</sub> (forsterite-fayalite). This is now done for the series Mg<sub>2</sub>SiO<sub>4</sub>—Mn<sub>2</sub>SiO<sub>4</sub> (forsterite-tephroite) and Mn<sub>2</sub>SiO<sub>4</sub>—Fe<sub>2</sub>SiO<sub>4</sub> (tephroite-fayalite). Previously published results, supplemented by some new optical determinations, are tabulated and plotted. Passing along the linear series Mg<sub>2</sub>SiO<sub>4</sub>—Mn<sub>2</sub>SiO<sub>4</sub>—Fe<sub>2</sub>SiO<sub>4</sub>, there is a gradual diminution in the optic axial angle and an increase in the refractive indices, but the latter, when plotted against the composition, do not lie along a straight line.

L. J. S.

**Belgian Minerals.** H. BUTTGENBACH (*Ann. Soc. Géol. Belgique*, 1919, **42**, *Mém.* 93—124).—Crystallographic and optical determinations were made on hopeite, apophyllite, hemimorphite, barytes, anglesite, lepidolite, fuchsite, aragonite, gypsum, and calcite from various localities in Belgium. A brown clay, from Furfooz, with waxy lustre, easily breaking into irregular fragments with conchoidal fracture, unctuous, and adhering to the tongue, has H a little more than 2 and D 2.05. Before the blowpipe it decrepitates, and in the closed tube gives off water and blackens. In water, it breaks up with a slight noise and slowly falls to powder, but does not make a paste. It is, in part, soluble in acids. These characters, as well as the following analysis, point to bole.

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	P <sub>2</sub> O <sub>5</sub> .	Ign.	Total.
38.67	27.13	11.25	1.15	1.10	1.34	19.34	99.98

The portion (24.21%) soluble in acids contains Al<sub>2</sub>O<sub>3</sub> 7.67 and Fe<sub>2</sub>O<sub>3</sub> 9.36%. Deducting these as bauxite (Al<sub>2</sub>O<sub>3</sub>.2H<sub>2</sub>O) and limonite, the remainder corresponds in composition with a mixture of halloysite and opal.

A whitish efflorescence on the coal shale of the Bois-l'Evêque colliery, near Liège, is found on optical examination to consist mainly of trona (3Na<sub>2</sub>O.4CO<sub>2</sub>.5H<sub>2</sub>O). Recalculating an old analysis (Malaise, 1881) of this material and deducting the sulphate as thenardite or as mirabilite, gives, however, a remainder with the composition 3Na<sub>2</sub>O.3CO<sub>2</sub>.13H<sub>2</sub>O or 3Na<sub>2</sub>O.3CO<sub>2</sub>.11H<sub>2</sub>O.

L. J. S.

**The Richardton Meteorite.** T. T. QUIRKE (*J. Geol.*, 1919, **27**, 431—449).—This meteorite belongs to the veined spherical chondrite class (Cca) of Brezina's classification. Under the microscope these stones reveal a composition of olivine, monoclinic pyroxene, glass, metallic iron, and troilite. A notable characteristic is the veining. The veins are not continuous, and consist largely of troilite and metallic iron and nickel. In most cases the metal and sulphide are mingled in a manner to suggest contemporaneous deposition or concentration. A few specks of metallic copper were noted in the troilite. An analysis showed: metallic portion 19.90%, silicate portion 80.10%. The metallic portion gave: Fe 90.89, Ni 8.92, Co 0.15, P 0.04%. The silicate portion yielded: SiO<sub>2</sub> 44.49, TiO<sub>2</sub> 0.10, Al<sub>2</sub>O<sub>3</sub> 2.46, Cr<sub>2</sub>O<sub>3</sub> 0.64, Fe<sub>2</sub>O<sub>3</sub> 4.34, P<sub>2</sub>O<sub>5</sub> none, MnO 0.19, FeO 16.23, CaO 2.69, MgO 28.32, Na<sub>2</sub>O 0.85, K<sub>2</sub>O 0.165%. These analyses were made from fragments representative of the matrix, and not on the vein material. It is estimated that about 90 kilos. of material have been recovered, the largest single piece weighing 8.7 kilos.

CHEMICAL ABSTRACTS.

## Analytical Chemistry.

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### A Cheap Substitute for Platinum Wire for Flame Tests.

A. EHRLINGHAUS (*Centr. Min.*, 1919, 192).—The platinum wire used for carrying out flame tests can be simply and cheaply replaced by a strip of filter paper. To test a solution, a strip of pure filter paper is folded several times, and one end dipped in the solution. The damp end is then held in the outer flame of a Bunsen burner. If an insoluble salt is to be tested, the strip is first dipped in dilute hydrochloric acid, and a little of the salt is then sprinkled on the damp end. In either case, a good, pure flame coloration is obtained, which lasts as long as the paper is prevented from burning by the moisture or the salt. A lasting, monochromatic flame can be obtained by dipping one end of a strip of paper in a vessel containing the dissolved salt, the other end being held in the Bunsen flame. The paper is prevented from burning by a crust of salt, which soon forms.

E. H. R.

### Use of certain Indicators. Sensitised Sodium Alizarinsulphonate.

W. MESTREZAT (*J. Pharm. Chim.*, 1920 [vii], 21, 185—192).—Sensitised sodium alizarinsulphonate (prepared by neutralising the commercial product, which is nearly always alkaline in reaction) is a sensitive indicator for use in the titration of mineral acids, oxalic acid, and alkali hydroxides, and possesses the advantage over phenolphthalein and litmus that it can be used for the titration of both ammonia and phosphoric acid; it cannot, however, be used in the presence of carbonates.

W. P. S.

### Modified Orsat Apparatus.

THOS. B. SMITH (*Gas World*, 1919, 71, 379).—The gaseous mixture is passed under the maximal pressure of the reservoir through a platinum capillary tube, 13 cm. long and 1.6 mm. in external diameter, which is raised to a white heat, into an additional absorption pipette filled with water. The mixture is thrice returned and re-passed through the capillary, whereby combustible gases are completely burnt. The resultant mixture of carbon dioxide, oxygen, and nitrogen is analysed in the usual manner.

CHEMICAL ABSTRACTS.

### Improved Method of, and Apparatus for, Detecting Water Vapour or either of the Gaseous Components thereof.

HENRY EDWARD FANE GOOLD-ADAMS, WILLIAM HENRY BOUSFIELD, and GEORGE WILLIAM TODD (*Brit. Pat.* 137547).—The gases suspected of containing water vapour, or either oxygen or hydrogen, which must first be converted into water by passing over a suitable catalyst, are passed over a salt, such as an alkali chloride or nitrate, which forms part of an electric circuit. If the partial pressure of the water vapour exceeds the critical hydration pressure of the particular salt

selected, it takes up moisture and allows a current to pass in the circuit, whereby a suitable indication may be given by means of a galvanometer or an electric bell operated by a relay. The salt is conveniently placed between a pair of wire gauze electrodes, through which the gases are passed. The device is particularly applicable in cases where it is necessary to provide against an explosive mixture of oxygen and hydrogen in gaseous reactions, such as in the synthetic production of ammonia, in which cases a continuous sampling of the mixed gases is secured by means of a by-pass, and a salt is selected of which the hydration pressure is approximately equal to the partial pressure of the aqueous vapour corresponding with the percentage of oxygen, against which a warning is required.

G. F. M.

**Short Modification of the Official Method of Estimating Chlorine in Foods, Fæces, and Urine.** J. O. HALVERSON and E. B. WELLS (*J. Biol. Chem.*, 1920, **41**, 205—208).—The complete washing out of the excess of silver nitrate from the silver chloride precipitate is eliminated, and, instead, an aliquot portion of the direct filtrate is titrated with ammonium thiocyanate. It is recommended that the reagents for titration be 0.05*N*.

J. C. D.

**The Oxidation-potentiometric Titration of Iodides in the Presence of Chlorides and Bromides.** I. M. KOLTHOFF (*Rec. trav. chim.*, 1920, **39**, 208—214).—Using the method of titration previously described (A., 1919, ii, 352), iodides may be estimated in the presence of any quantity of chlorides or of relatively large amounts of bromides, by titration with potassium dichromate, or, preferably, potassium bromate or iodate, the titration being carried out in the presence of hydrochloric acid.

W. G.

**Estimation of Oxygen by the Copper-Ammonia-Ammonium Chloride Reagent.** W. L. BADGER (*J. Ind. Eng. Chem.*, 1920, **12**, [2], 161—164).—Hempel's method for the absorption of oxygen by means of metallic copper spirals covered with a solution containing equal parts of saturated ammonium carbonate solution and ammonia (D 0.93) was the basis for a series of experiments in which varying strengths of ammonia, and salts of ammonia other than the carbonate, were used. The results were compared by determining in each case the specific absorption as defined by Anderson. Specific absorptions were found of 22.5 vols. with a concentrated ammonia solution (D 0.90) saturated with ammonium chloride, 45—47 vols. with a mixture of two parts of concentrated ammonia and one of water saturated with ammonium chloride, 55—60 vols. with a mixture of one part of concentrated ammonia and one of water saturated with ammonium chloride, and 30 vols. with a mixture of one part of concentrated ammonia and two of water saturated with ammonium

chloride. The author concludes that an improvement on Hempel's method is obtained by using a solution prepared by saturating a mixture of one part of concentrated ammonia and one of water with ammonium chloride. This solution may be used to absorb fifty to sixty times its volume of oxygen, after which, although its absorption capacity is not exhausted, the amount of precipitate formed makes the solution unworkable. It is claimed that this reagent is cleaner and has a longer life than alkaline pyrogallol; unlike phosphorus, it is unaffected by catalysts, is readily prepared, and is active at almost any temperature. On the other hand, it cannot be used for mixtures containing carbon monoxide or acetylene, and when fresh it is liable to leave measurable amounts of ammonia in the gas. S. S. A.

**The Estimation of Nitrogen in Nitrocellulose and Inorganic Nitrates with the Nitrometer.** ERNEST GEORGE BECKETT (T., 1920, 117, 220—235).

**Estimation of Phosphoric Acid as Ammonium Phosphomolybdate.** A. STUTZER (*Landw. Versuchs. Stat.*, 1919, 94, 251—264).—Conditions are given under which phosphoric acid may be estimated by precipitating it as ammonium phosphomolybdate and weighing the precipitate directly. The precipitation is made in a nitric acid solution containing a small quantity of sulphuric acid, and the precipitate, after being collected on a weighed asbestos filter, is washed first with 2% ammonium nitrate solution, then with alcohol or acetone, dried at 100° for one hour, and weighed. The weight of the precipitate is multiplied by 0.03513 to obtain the amount of  $P_2O_5$ . [See, further, *J. Soc. Chem. Ind.*, 1920, 250A.] W. P. S.

**Estimation of Arsenic in Organic Compounds such as Salvarsan.** L. JOSLYN ROGERS (*Can. Chem. J.*, 1919, 3, 398).—The sample, 0.5 gram, dissolved in 10 c.c. of water, is treated with 5 c.c. of nitric acid, heated on the hot plate, and solid ammonium persulphate is added until the mixture is colourless; a yellow coloration, if persistent, can be removed by boiling for a few minutes after the addition of a few c.c. of water and several grams of ammonium persulphate all at once. The volume is made up to 100 c.c., 5 c.c. of saturated sodium ammonium hydrogen phosphate solution are added, followed by an excess of magnesia mixture; any precipitate which forms is dissolved by dilute nitric acid. The solution is heated nearly to the b. p., an excess of aqueous ammonia is added, and, after cooling and keeping for two hours, the precipitate is collected, washed with dilute aqueous ammonia, returned, together with the filter, to the precipitation flask, and dissolved in 70 c.c. of dilute hydrochloric acid (three parts of acid to two parts of water). The solution is cooled, shaken for one minute with 3 grams of potassium iodide dissolved in

6 c.c. of water, 70 c.c. of water are then added, and the liberated iodine titrated at once with thiosulphate.

## CHEMICAL ABSTRACTS.

**Detection of Arsenic in Salvarsan and Neosalvarsan.**

F. UTZ (*Pharm. Zentr.-h.*, 1920, **61**, 39—42).—The substance is decomposed by heating with a small quantity of sulphuric acid and ammonium persulphate, or with hydrogen peroxide and ferrous sulphate, the solution then diluted, and treated with stannous chloride solution. After a time, the arsenic forms a brown, flocculent precipitate. When a portion of either substance is dissolved in dilute hydrochloric acid in a platinum basin, and a fragment of zinc is added, a brown stain is obtained on the platinum surface. Another test consists in dissolving the substance in concentrated sodium thiosulphate solution and adding hydrochloric acid; sulphur is precipitated, and this is soon coloured bright yellow by the precipitation of arsenic sulphide, which may be separated and identified by the stannous chloride test.

W. P. S.

**Renovation of Combustion Tubes.** J. DORSMAN (*Chem.*

*Weekblad*, 1920, **17**, 132).—Combustion tubes which have been used for the analysis of substances containing halogens may be renovated as follows. A wash-bottle filled with water is connected to one end of the tube. To the other end an empty U-tube is fitted, connected to a pump. A stream of moist air is drawn through the tube while still red hot. Copper halogen compounds and iodine condense in the cold end and in the U-tube. These may be removed by a piece of wet filter paper. When no further condensation takes place, dry air is drawn through the tube, which is then ready for further use.

W. S. M.

**Use of Soda-lime in the Calcium Chloride Tube of the Potassium Hydroxide Absorption Apparatus.** J. FRIEDRICH

(*Zeitsch. angew. Chem.*, 1919, **32**, 363—364).—Further experiments with gaseous mixtures containing varying proportions of carbon dioxide have confirmed the previous conclusion (this vol., ii, 192) that the use of soda-lime in the calcium chloride tubes of a potassium hydroxide absorption vessel is not only superfluous, but may even be disadvantageous, leading to loss of water. The general belief that potassium hydroxide solution absorbs carbon dioxide less efficiently than soda-lime is probably attributable to the use of absorption apparatus with calcium chloride tubes of insufficient length. The loss of moisture depends on the tension of the absorption agent, the velocity of the gas and the duration of absorption, and is proportional to the last two factors. For the amount of gas evolved in an ordinary elementary analysis, a short calcium chloride tube is sufficient, and no loss of moisture can be observed when the tube is half filled with soda-lime; but in the analysis of carbonates, loss of water is inevitable under such

conditions, and the current of air must be continued for a long time to remove the whole of the carbon dioxide. Similar conditions occur in the estimation of carbon in iron. The dimensions of a calcium chloride tube suitable for this purpose are: length 4 cm. and diameter 0.8 cm. About  $1\frac{1}{2}$  grams of calcium chloride are sufficient to dry the gaseous mixture leaving the potassium hydroxide apparatus, provided that this is charged with potassium hydroxide solution (2:3), that the velocity of the gas does not exceed 0.3 c.c. per second, and that the duration of the absorption does not exceed three hours.

C. A. M.

**Method for the Preparation of a Hydrochloric Acid Solution of Cuprous Chloride for use in Gas Analysis.**

F. C. KRAUSKOPF and L. H. PURDY (*J. Ind. Eng. Chem.*, 1920, **12**, 158—161).—A solution of stannous chloride was prepared by heating on a sand-bath, to slow boiling, 300 grams of metallic tin contained in a 500 c.c. flask and covered with concentrated hydrochloric acid, a small amount of fresh acid being added from time to time until the solution was saturated with stannous chloride. The solution was then filtered and stored in a flask containing metallic tin to prevent oxidation. A portion of this solution was mixed with cuprous chloride solution and concentrated hydrochloric acid to obtain a solution of cuprous chloride of approximately the same copper and acid content as a corresponding solution of cuprous chloride, free from other salts, prepared by reducing cupric chloride with copper in acid solution. The two solutions were compared by the absorption, in Hempel double pipettes, in the usual way, of carbon monoxide evolved from oxalic acid by the action of sulphuric acid. Figures were obtained which indicate that the efficiency of cuprous chloride solution for the absorption of carbon monoxide is not deleteriously affected by the presence of relatively large amounts of stannous and stannic chlorides; a satisfactory reagent is obtained by reducing cupric chloride in acid solution by means of stannous chloride, and if a small excess of stannous chloride is used, the solution may be exposed to air during transference from one vessel to another without becoming oxidised. Further, the solution may be renewed, after saturation with carbon monoxide, by heating at 60—70° to drive off the gas, a few drops of concentrated stannous chloride solution being added to correct any oxidation which might occur.

S. S. A.

**Estimation of Carbon Dioxide, Oxygen, and Combustible Gases by Krogh's Method of Micro-analysis.** HANS OLUF SCHMIT-JENSEN (*Biochem. J.*, 1920, **14**, 4—24).—It is shown that Krogh's micro-gas analysis apparatus may be used to estimate hydrogen and carbon monoxide in very small gas samples (*Skand. Arch. Physiol.*, 1908, **20**, 279). As absorbent for hydrogen, a solution of 0.66 gram of colloidal palladium and 0.42 gram of sodium picrate in 20 grams of distilled water is used, and as



absorbent for carbon monoxide an acid solution of cuprous chloride. A modification of Krogh's apparatus is described by means of which it is possible to estimate carbon dioxide and oxygen by absorption, hydrogen and methane by combustion, and carbon monoxide either by absorption or combustion. The hydrogen and methane can only be estimated by combustion if the bubble of gas has a volume of at least 80 cu. mm.; nitrogen is also taken by difference. The fractional combustion of hydrogen and methane is also possible by means of this apparatus. The average error in the readings is about  $\pm 0.1$  mm. This systematic error is different with the different gases, and in the case of oxygen, hydrogen, methane, and carbon dioxide is of no practical importance, but it must be taken into consideration with carbon dioxide. A small receiver for collecting gas samples is described. J. F. S.

**Direct Estimation of Potassium and Sodium in Small Quantities of Blood.** B. KRAMER (*J. Biol. Chem.*, 1920, 41, 263—274).—The method for potassium is a modification of the sodium cobaltinitrite method capable of being used for 1 c.c. of blood or 3—5 c.c. of plasma or serum. The sodium process is based on the precipitation of that element as the pyroantimonate, which is weighed as such. The potassium content of normal human serum varies between 16 and 22 mg. per 100 c.c. of serum. The sodium content has been found in both normal children and adults to vary between 280 and 310 mg. per 100 c.c. of serum. J. C. D.

**Estimation of Zinc in Organic Materials, such as Food, Urine, and Excrement. The Zinc Content of Reagents and Analytical Vessels.** A. WEITZEL (*Arb. Gesundh. Amt.*, 1919, 51, 476—493; from *Chem. Zentr.*, 1920, ii, 5—6).—Two methods are described for the estimation of zinc in organic substances. In the first of these, the material is converted into ash, either by the wet or dry process; the latter is dissolved in acid, copper, etc., is removed by hydrogen sulphide, and zinc is precipitated from the acid filtrate by potassium ferrocyanide. The zinc ferrocyanide is decomposed by concentrated sulphuric acid, zinc is precipitated in the usual manner with ammonium sulphide, the precipitate is dissolved in hydrochloric acid, and the zinc is again precipitated by hydrogen sulphide from acetic acid solution. The sulphide is finally dissolved in 1% hydrochloric acid, the zinc is precipitated with sodium carbonate, and weighed as the oxide. The second method is identical with the first as far as the separation of sulphides of copper, etc. Ferrous compounds are then oxidised by nitric acid, sodium hydroxide is added, and the disturbing effect of phosphates is overcome by acidification with acetic acid. The residue left on filtration is separated as completely as possible from the mother liquor and dissolved in dilute hydrochloric acid; it is again treated with sodium hydroxide and acetic acid, and, if necessary, the process is repeated until zinc can no

longer be detected in the acid filtrate by means of potassium ferrocyanide. The united acetic acid filtrates are saturated with hydrogen sulphide. The details of the two methods are minutely described in the original. Either process permits an exact estimation of zinc as oxide in urine, excrement, animal organs and tissues, and in foods, even if the metal is only present in minimal amounts. It is a matter of indifference whether the organic material is oxidised by the wet or dry process. The second method is to be preferred to the potassium ferrocyanide process, since it requires a smaller number and smaller amounts of reagents, and can be carried out in a shorter time. If the directions are closely followed, and pure reagents free from zinc are used, so little zinc passes into the material under investigation, either from the reagents or from the Jena-glass flasks, which contain considerable quantities of zinc, that it need not be taken into account even for the most accurate analyses. Otherwise, in those cases in which concentrated solutions of alkali hydroxide or phosphoric acid are boiled, or even small quantities of fluorides are warmed with mineral acids in vessels made of glass containing zinc, the possibility of the passage of zinc from the vessel into the material under investigation must always be taken into account; in these circumstances, the use of vessels made of glass free from zinc is advisable.

H. W.

**Estimation of Mercury in Organic Combination by means of Zinc Filings.** MAURICE FRANÇOIS (*J. Pharm. Chim.*, 1920, [viii], 21, 85—91).—A modification of a method described previously (A., 1918, ii, 276) is recommended. The substance is dissolved by heating with alcohol, and the solution is then treated with hydrochloric acid and zinc filings. With mercury benzoate and mercury salicylate, the reduction with zinc is carried out in sodium hydroxide solution containing potassium iodide, and any excess of zinc is dissolved subsequently by treatment with hydrochloric acid.

W. P. S.

**Estimation of Iron in Iron Ores by means of Permanganate.** L. BRANDT (*Chem. Zeit.*, 1920, 44, 101—103, 121—122).—Compare A., 1919, ii, 373, 480).—A further criticism of the method described by Schwarz and Rolfes (A., 1919, ii, 170). W. P. S.

**The Analysis of Wulfenite Earths from Mies.** E. DITTLER (*Centr. Min.*, 1919, 225—227).—A method has been devised by which calcium, lead, molybdenum, and zinc can be estimated in a single sample of the mineral. About a gram of the finely powdered material is digested successively with hydrochloric and nitric acid until the residue is no longer black. Digestion is then continued with sulphuric acid to convert the calcium and lead into sulphates, and the solution is diluted and filtered, the residue being washed several times with dilute sulphuric acid. The residue is then extracted with ammonium acetate solution, which dissolves both

calcium and lead. These are again precipitated as sulphates, weighed in a Neubauer platinum crucible, then dissolved in hydrochloric acid, the calcium precipitated as oxalate, and the lead estimated by difference. The acid solution containing the molybdenum and zinc is neutralised with ammonia, the iron present precipitated by addition of ammonium chloride and filtered, the solution made strongly ammoniacal, and saturated with hydrogen sulphide. The zinc sulphide is then salted out by addition of ammonium thiocyanate, and the molybdenum determined in the filtrate by known methods.

E. H. R.

**Separation of Zirconium and Titanium as the Phosphates.** JAMES BROWN and H. T. MADDEN (*J. Amer. Chem. Soc.*, 1920, **42**, 36—39).—Zirconium and titanium may be separated and estimated by the following method. The solution, containing 1—2% by volume of sulphuric acid, is treated with an excess of hydrogen peroxide, and then with an excess of disodium or diammonium phosphate, and the solution kept overnight. The precipitated zirconium phosphate is collected and washed with water containing a few drops of sulphuric acid and a little hydrogen peroxide. If, as is usually the case, the precipitate is coloured yellow by titanium, it is fused with sodium carbonate, extracted with water, and redissolved by fusing with potassium hydrogen sulphate, and then treating with dilute sulphuric acid. The zirconium is then reprecipitated as above, and if the precipitate is colourless, all the titanium has been removed. The zirconium phosphate is now converted into oxide by fusing with sodium carbonate, extracting with water, dissolving the residue in hydrochloric acid, and precipitating with ammonia. The precipitate is washed, dried, ignited, and weighed as the dioxide. The combined filtrates from the zirconium precipitation are boiled to decompose hydrogen peroxide, and the acidity adjusted so that the content of sulphuric acid is about 2% by volume. An excess of disodium or diammonium phosphate is added, the mixture kept for one hour, and then filtered. The precipitate of titanium phosphate is washed, converted into the dioxide, as in the case of zirconium, and weighed. The results given in the paper show that the method is capable of a high degree of accuracy.

J. F. S.

**Testing of Chloroform.** F. Utz (*Pharm. Zentr.-h.*, 1917, **58**, 1—5).—The author has investigated, in particular, the benzidine test for the detection of decomposition products in chloroform. When benzidine is dissolved in pure chloroform, the solution remains unchanged for twenty-four hours if kept in a dark place; if chloral is present, a faint red coloration develops at first, and changes to bluish-red after a time. A turbidity forms immediately if the chloroform contains carbonyl chloride, hydrochloric acid, or chlorine, and a flocculent precipitate may separate.

W. P. S.

**The Reduction of Aromatic Nitro-compounds by Stannous Chloride and by Titanous Chloride, and their Volumetric Estimation.** DANIEL FLORENTIN and HENRI VANDENBERGHE (*Bull. Soc. chim.*, 1920, [iv], 27, 158—166).—The estimation of nitro-groups by reduction with stannous chloride and titration of the excess of the latter with iodine solution in neutral or acid medium (compare Altmann, A., 1901, ii, 475; Druce, A., 1919, ii, 199), gives satisfactory results with nitrobenzene and various di- and tri-nitro-derivatives, but, contrary to the results obtained by Druce (*loc. cit.*), the authors find that the results obtained for the mononitrotoluenes are too low, owing to the formation of *p*-chlorotoluidines.

Titanous chloride quantitatively reduces the nitro-compounds according to the equation  $C_6H_5 \cdot NO_2 + 6TiCl_3 + 6HCl = C_6H_5 \cdot NH_2 + 6TiCl_4 + 2H_2O$ , except in the case of *o*-nitrotoluene, which gives results which are about 3% too low. The excess of titanous chloride is determined by titrating it into a known volume of standard ferric sulphate solution, using ammonium thiocyanate as an indicator.

W. G.

**Differentiation of Methyl and Ethyl Alcohols.** TH. SABALITSCHKA (*Pharm. Zentr.-h.*, 1920, 61, 78—79).—Although the copper sulphate test (compare Pannwitz, this vol., ii, 62) has a limited use for the detection of methyl alcohol in ethyl alcohol in the absence of water, it is untrustworthy in the case of dilute alcohols.

W. P. S.

**The Estimation of Incompletely Nitrated Phenol in the Mother Liquors from Picric Acid by means of Bromine.** M. MARQUEYROL and P. CARRÉ (*Bull. Soc. chim.*, 1920, [iv], 27, 127—138).—The results obtained by Jolibois's method, by the action of bromine on the incompletely nitrated phenol in the mother liquors from picric acid are inaccurate and variable. The results obtained are too high, and vary with the time and temperature of contact of the bromine with the mother liquors and the amount of bromine in excess. It is shown that these mother liquors contain a mixture of sodium 2:4-dinitrophenol-*o*-sulphonate and sodium 2:6-dinitrophenol-*p*-sulphonate in variable proportions, together with some sodium nitrophenolsulphonate. The action of the bromine on each of the dinitrophenolsulphonates varies with the conditions given above; the mononitrophenolsulphonates tend to give dibromo-derivatives, and any picric acid remaining in the mother liquors is acted on by the bromine, all of these changes tending to vitiate the results obtained by Jolibois's method.

W. G.

**The Estimation of Incompletely Nitrated Phenol in the Mother Liquors from Picric Acid; the Ratio between the Composition of these Mother Liquors and the Yield of a Manufacture of Picric Acid.** M. MARQUEYROL and P. CARRÉ (*Bull. Soc. chim.*, 1920, [iv], 27, 138—140).—Marqueyrol and

Loriette's method is slightly modified. The mother liquors are completely nitrated, and the resulting picric acid is collected and estimated volumetrically by titration with *N*/10-sodium hydroxide. It is necessary to apply a correction for the amount of picric acid dissolved in the water with which the precipitate is washed. [See, further, *J. Soc. Chem. Ind.*, 1920, 248A.]

W. G.

**Estimation of Traces of  $\beta\beta'$ -Dichloroethyl Sulphide [Mustard Gas] in Air.** MAX YABLIK, G. ST. J. PERROT, and N. H. FURMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 266—274).—The method is based on the observation that a solution of selenious acid in sulphuric acid (1:1) is reduced by traces of  $\beta\beta'$ -dichloroethyl sulphide, giving an orange-red suspension of selenium; the presence of about 0.005 mg. of dichloroethyl sulphide can be detected in this manner. The estimation of the vapour in air is effected by bubbling the mixture through a suitable absorbent, such as a 1% solution of selenium dioxide in water, adding 10 c.c. of a solution of selenious acid in sulphuric acid, care being taken to use the latter in such a manner that a 1:1 solution is finally obtained, and also that the concentration of selenious acid in the ultimate mixture is the same as in the absorbing mixture. The solution is then heated for ten minutes in a bath at 85°, cooled, and the strength estimated by nephelometric comparison with standard solutions prepared from weighed quantities of the reagents. The process is available for amounts of substance between 0.1 mg. and 0.01 mg., with a maximum error of 0.005 mg. The temperature at which the solution is heated in process of "developing" can vary 5° in either direction without affecting the character of the suspension. The method is remarkably free from the necessity for extreme purity of original solution, cleanliness of glassware, etc., which obtains in silver haloid nephelometry. It was not found possible to use good solvents for dichloroethyl sulphide as absorbing media, and then determine the strength of the solutions by the proposed method, since the only suitable solvent (alcohol and acetic acid) reduced the selenious acid to some extent. The selenious reagent is not specific to mustard gas; arsine and the substituted arsines, and several other toxic gases, react with it vigorously.

Attempts to determine the strength of the suspension colorimetrically were not successful.

H. W.

**The Nephelometric Values of Cholesterol and the Higher Fatty Acids. II.** F. A. CSONKA (*J. Biol. Chem.*, 1920, **41**, 243—249).—The nephelometric values of oleic acid and cholesterol were found to be influenced by the hydrolysis, as well as by the addition of certain substances which alone, in similar circumstances, do not produce any turbidity. These influencing agents are exemplified by the use of gelatin as a protective colloid.

J. C. D.

**Formation of  $\beta$ -Methylumbelliferone as a Reaction of Acetoacetic Acid and its Esters.** VICTOR ARREGUINE and EDOUARD D. GARCIA (*Ann. Chim. anal.*, 1920, [ii], **2**, 36—41, *Anal. Soc. Quim. Argentina*, 1919, **7**, 424—432).—In hydrochloric acid solution, acetoacetic acid condenses with resorcinol to form  $\beta$ -methylumbelliferone, and the latter exhibits an intense blue fluorescence when the solution is rendered slightly ammoniacal. To make the test, 2 c.c. of hydrochloric acid containing a trace of acetoacetic acid or ethyl acetoacetate and 0.1 gram of resorcinol are boiled for a few minutes, cooled, diluted with water, and treated with a slight excess of ammonia. In the case of urine, 50 c.c. of the sample are treated with three drops of hydrochloric acid and extracted first with 5 c.c. and then with 3 c.c. of carbon tetrachloride; the latter solution is evaporated to about 3 c.c., and then tested as described. The test will detect 0.00002 gram of acetoacetic acid in 5 c.c. of urine. The reaction is specific, and is not given by acetone or  $\beta$ -hydroxybutyric acid.

W. P. S.

**Estimation of Acetone and Acetoacetic Acid with Autenreith's Colorimeter.** EMIL LENK (*Münch. med. Woch.*, 1919, **66**, 1119—1120; from *Chem. Zentr.*, 1919, iv, 995).—A reply to Schall (this vol., ii, 63), in which it is pointed out that the latter has simply adopted the author's method with the substitution of Autenreith's colorimeter for a measuring cylinder.

H. W.

**Analysis of Acetone by Messinger's Method.** LEO FRANK GOODWIN (*J. Amer. Chem. Soc.*, 1920, **42**, 39—45).—Messinger's method for the analysis of acetone (A., 1889, 313) has been critically investigated. The method consists in shaking acetone in the presence of alkali hydroxide with an excess of iodine. After ten minutes, the solution is acidified, and the excess of iodine titrated with a standard solution of sodium thiosulphate. It is shown that under proper conditions the method gives accurate and concordant results. The effect of keeping, the method of shaking and adding the iodine solution, the effect of an excess of acid, and the dilution have all been investigated and found to be without influence on the results. It is shown that methyl and ethyl alcohol if present both use up a certain amount of iodine.

J. F. S.

**The Acetone Concentration in Blood, Urine, and Alveolar Air. I. A Micro-method for the Estimation of Acetone in Blood, Based on the Iodoform Method.** ERIK MATTEO PROCHET WIDMARK (*Biochem. J.*, 1919, **13**, 430—445).—The blood is drawn from the finger or ear lobe into a capillary pipette graduated to 100 c.mm., and is then transferred into the flask of the distillation apparatus, in which there has previously been placed 10 c.c. of 1% phosphoric acid. The pipette is washed out several times with the acid. The distillation must be carried out within two or three hours of the drawing of the blood, and the distillate is collected in a cooled test-tube containing 3 c.c. of

*N*/2-sodium hydroxide and 2 c.c. of *N*/200- or *N*/100-iodine solution, according to the amount of acetone. The residual iodine is titrated with equivalent sodium thiosulphate after the contents of the tube have been treated with 3.5 c.c. of *N*/2-sulphuric acid. The presence of ethyl alcohol in the blood has no effect on the results of the titration. As a micro-method, the process is not applicable to normal blood and urine, but gives trustworthy results in pathological conditions where there is an increased amount of acetone in these fluids.

J. C. D.

**Estimation of Acetone Substances.** N. O. ENGFELDT (*Acta med. scand.*, 1919, **52**, 311—366; from *Chem. Zentr.*, 1920, ii, 161—162).—Salén's proposed modification (*Nord. med. ark. avd.*, 1918, ii, **51**, No. 11) of the author's previous method for the estimation of acetone substances in urine is unsatisfactory, since errors of 24.5—41.5% occur. Recent investigations lead to a modification of the method, which is now carried out in the following manner. Precipitation of the urine is effected with ammonia, lead acetate, and alum in an exactly specified manner, and, after dilution and acidification with concentrated sulphuric acid, the acetone is distilled and the distillate is titrated with iodine. Chromate and sulphuric acid are added, and the residue is again distilled; the iodine required is a measure of the  $\beta$ -hydroxybutyric acid. Another estimation, in which, first, concentrated sulphuric acid, and then, shortly afterwards, chromate and sulphuric acid are added, permits the measurement of the total acetone substances of the urine as acetoacetic or  $\beta$ -hydroxybutyric acid by one distillation which can be performed in twenty-five minutes. It should be noted that the presence of alcohol in urine, arising from fermentation of dextrose or imbibed by the patient, disturbs the estimation. Toluene, which is more soluble in urine than in distilled water, is, in 2.5% concentration, an active disinfectant, and is recommended as a preservative, since it does not interfere with the estimation.

The author has elaborated a somewhat similar clinical method for the estimation of acetone substances in blood, the details of which will be published shortly.

H. W.

**Estimation of Dextrose in the Presence of Lactose.** E. HILDT (*J. Pharm. Chim.*, 1920, [vii], **21**, 136—137; *Ann. Chim. anal.*, 1920, [ii], **2**, 78—80; *Ann. Falsif.*, 1920, **13**, 21—25).—A Fehling's solution is used. 10 c.c. of which correspond with 0.048 gram of dextrose and 0.071 gram of lactose hydrate or 0.051 gram of lactose after hydrolysis. The solution containing the two sugars is titrated direct into 10 c.c. of the Fehling's solution, and again after hydrolysis. For the hydrolysis, an amount of the sugar solution containing not more than 1 gram of lactose is heated for six hours at 95—98° with 20 c.c. of an 18% solution of sodium benzenesulphonate in *N*-sulphuric acid, after making the mixture up to 100 c.c. with distilled water.

W. G.

**Estimation of Sugar in Diabetic Blood.** G. VIGEVANI (*Boll. Chim. farm.*, 1919, **58**, 436—439).—Two c.c. of the blood are mixed with 100 c.c. of potassium chloride solution (saturated potassium chloride solution 340 c.c., hydrochloric acid 0.375 c.c., and water 160 c.c.), 50 c.c. of the mixture boiled for five minutes, filtered from the precipitated proteins, the filtrate made up to definite volume, and 10 c.c. introduced into an Erlenmeyer flask, round the neck of which rubber tubing has been fixed. From 1 to 2 c.c. (according to the amount of dextrose) of a copper solution (copper sulphate 2.2, potassium hydrogen carbonate 80, potassium carbonate 50, potassium chloride 53 grams; water, 500 c.c.) are added, the mixture boiled for three minutes, and the rubber tube closed with a clip, so that a vacuum is produced within the flask after cooling. A current of carbon dioxide is then introduced, and the liquid titrated with iodine solution (*N*/10-hydrochloric acid 5 c.c., iodine 0.0635 gram, potassium iodide 2 grams, 2% potassium iodate solution 2 c.c., and water to 100 c.c.), with starch solution (2 grams of soluble starch in 100 grams of saturated potassium chloride solution) as indicator. The copper reduced by the dextrose reacts with the iodine solution. The latter is previously standardised on pure dextrose which has been dried at 100°. C. A. M.

**Method of Identification of Amino-acids.** SHINTARO KODAMA (*J. Tokyo Chem. Soc.*, 1919, **40**, 743—754).—The principle of the method, which in this paper deals only with phenylalanine, consists in converting the amino-acid into the hydroxy-acid and determining the m. p. of the latter.

A solution of 0.2—0.3 gram of phenylalanine in a slight excess of acid (preferably sulphuric acid) is treated at 80° with a solution of sodium nitrite very slowly until nitrogen ceases to be evolved. The solution is boiled for two to three minutes, diluted with water to twice or thrice its volume, boiled with calcium carbonate for twenty to thirty minutes, filtered, and concentrated to 5—7 c.c. Calcium phenyl-lactate is precipitated by the addition of a few drops of 2*M*-calcium chloride. The phenyl-lactate is dissolved in 2 c.c. of concentrated hydrochloric acid, and the m. p. of the phenyl-lactic acid which separates after several hours is determined after recrystallisation from alcohol or benzene.

The author has isolated another hydroxy-acid, m. p. 93—94°, mol. wt. 176, which is very strongly laevorotatory, and is probably derived from an isomeride of phenylalanine.

The phenylacetaldehyde obtained by heating 0.01 gram of phenyl-lactic acid develops with 2—3 c.c. of 50% alcoholic sulphuric acid a permanent, green coloration after keeping for several hours.

CHEMICAL ABSTRACTS.

**Detection of Carbamide.** J. F. A. POOL (*Pharm. Weekblad*, 1920, **57**, 178—179).—The presence of the enzyme urease may be detected in soja beans by means of the colour effects produced in a jelly containing 2% of carbamide and aqueous yeast extract (A.,



1916, i, 536). Conversely, the presence of carbamide in solutions may be shown by making the liquid neutral to phenolphthalein, adding 2% of agar-agar, boiling, and placing a small section of soja bean on a portion of the jelly solidified in a watch-glass. After some time a red coloration begins to spread from the bean outwards.

W. S. M.

**Method of Estimating Quinine and Strychnine when Occurring in Common Solution.** A. R. BLISS (*J. Amer. Pharm. Assoc.*, 1919, 8, 804—807).—The method is based on the solubility of strychnine in water (1 in 6420) and its slight solubility in ethyl ether. Fifty c.c. of the preparation are freed from alcohol, a slight excess of citric acid is added, followed by an excess of aqueous ammonia, the total alkaloids are extracted by chloroform-ether mixture, the extract is evaporated, and the residue is dried and weighed. The total alkaloids are dissolved in dilute sulphuric acid, an excess of water (more than 6500 times the weight of the strychnine) is added, together with an excess of aqueous ammonia, and the mixture is shaken seven times with ether. The ethereal extracts are united, washed with 5 c.c. of water and evaporated, and the residue is dried and weighed as quinine. The residual aqueous solution is extracted seven times with chloroform, the extracts are united and evaporated, and the residue is dried and weighed as strychnine. Excellent results are recorded for solutions of approximately known strength.

CHEMICAL ABSTRACTS.

**A Modification of the Francis-Connell Method of Estimating Hydrocyanic Acid.** PAUL MENAUL and C. T. DOWELL (*J. Agric. Res.*, 1920, 18, 447—450).—See this vol., i, 359.

**The Toxicological Detection of Physostigmine [Eserine].** H. FÜHNER (*Biochem. Zeitsch.*, 1918, 92, 347—355).—Quantities of 5/1000—1/100 mg. of eserine can be detected by means of the biological eye reaction in the cat. The author finds that in the case of the plain muscle of the leech, minute quantities of eserine in the presence of acetylcholine increase the contraction of the muscle brought about only to a small extent by acetylcholine alone. By this joint action of the two drugs on the muscle of the leech, 1/10,000 mg. of eserine can be detected with certainty. S. S. Z.

**A Quantitative Biological Method for the Estimation of Nicotine.** H. FÜHNER (*Biochem. Zeitsch.*, 1918, 92, 355—364).—By means of the contraction produced by the action of nicotine on the plain muscle of the leech, it is possible to estimate quantitatively 1/100 mg. of the drug. The myograph of the nicotine solution of unknown strength is compared with that of a solution of known strength.

S. S. Z.

## General and Physical Chemistry.

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**Perturbation Theory of the Helium Atom.** A. LANDÉ (*Physikal. Zeitsch.*, 1920, **21**, 114—122).—A purely mathematical paper, deducing the series spectra of helium by the consistent application of the quantum theory to a system of two electrons revolving round a nucleus of charge  $+2e$  in circular and elliptical paths, co-planar and inclined. F. S.

**The K-Absorption Bands of Rare Earths for X-Rays.** M. DE BROGLIE (*Compt. rend.*, 1920, **170**, 725).—The author has obtained the  $K$  bands for the elements numbered 69, 70, 71. The band of lutecium is placed between the two groups  $K_a$  and  $K_b$  of tungsten. Approximate measurements give the  $K$  band of thulium ( $N=69$ ) at  $\lambda=0.208 \times 10^{-8}$ , of neoytterbium ( $N=70$ ) at  $\lambda=0.2015 \times 10^{-8}$ , and of lutecium ( $N=71$ ) at  $\lambda=0.195 \times 10^{-8}$ . W. G.

**The Constitution of Atmospheric Neon.** F. W. ASTON (*Phil. Mag.*, 1920, [vi], **39**, 449—455).—The observation in 1912 by Sir J. J. Thomson of a faint but unmistakable parabola corresponding roughly with an atomic weight 22, in addition to the expected one at 20, in the positive ray spectrum of neon, and the absence of any parabola at 22 except in presence of neon, was strong evidence of the line being due to an isotope of neon. Fractional distillation failed to effect any separation, and diffusion results, although more hopeful, have failed to be conclusive. A difference of 0.7% in density in the first set of experiments could not be repeated in more elaborate ones, 0.3% difference only being obtained. By new and refined methods of positive-ray analysis, exact measurements have shown that the atomic weight of the two constituents in neither case corresponds exactly with that of neon, 20.2. Four parabolas corresponding with the doubly and singly positively charged atoms of the two isotopes have been carefully measured. The corrected results gave for the one constituent ( $\text{Ne}^a$ ) an atomic weight of 20.00, and for the other ( $\text{Ne}^b$ ) 22.00, to an accuracy of about 0.1%. The intensities of the lines were in agreement with the required 90% to 10% ratio. On the clearest spectra there was evidence of a third isotope of mass 21, extremely faint, and probably not present to the extent of 1%. F. S.

**Radioactive Disintegration Products in the Free Atmosphere and the Probability of their Origin being the Sun.** HERMANN BONGARDS (*Physikal. Zeitsch.*, 1920, **21**, 141—145).—The radioactivity of a wire suspended at a mean height of 1500 metres, under the influence of the earth's field, has been determined. It is shown that a relationship exists between the activity,

the air pressure at the earth's surface, and the potential temperature in the air layer between 1000 and 2500 metres. A well-defined parallelism is observed between the activity and the temperature in this air layer. The temperature changes are regarded as the cause of the pressure changes. Since the influence of the radioactive substances on the temperature cannot occur to the observed extent, and since temperature is without influence on the activity, it is assumed that a radiation of material from a definite and restricted portion of the sun is the cause of the observed effects. This radiated matter carries with it the emanation particles which are observed in the atmosphere. The heat action of the material radiations constitutes the chief source of heat of the higher layers of the atmosphere. J. F. S.

### Intermolecular Change of Place of Similar Atoms.

GEORG VON HEVESY and LÁSZLÓ ZECHMEISTER (*Ber.*, 1920, 53, [B], 410—415. Compare von Hevesy and Rona, A., 1915, ii, 247).—By employing radioactive methods, the authors show that intermolecular change of place occurs between lead atoms to an extent which can be exactly calculated from the law of probability when they are in an ionised state; organically combined lead atoms are not subject to similar transposition in homogeneous phase. Thus, when activated lead nitrate and inactive lead chloride are dissolved in molar proportions in boiling pyridine, and the solution is kept hot for some time and then allowed to cool, the lead chloride which separates is found to be exactly half as radioactive as the original specimen of lead nitrate. Similar results are obtained with the following pairs of compounds: lead formate (active) and lead acetate in water; plumbous acetate (active) and plumbic acetate in glacial acetic acid; plumbic acetate (active) and plumbous acetate in glacial acetic acid. Interchange does not occur with lead chloride (active) and lead tetraphenyl in pyridine, with lead acetate (active) and lead tetraphenyl in amyl alcohol, or with lead nitrate (active) and lead diphenyl nitrate in dilute ethyl alcohol. H. W.

### Radioactivity of the Rocks of the Kolar Gold Fields.

HERBERT EDMESTON WATSON and GOSTABEHARI PAL (*J. Ind. Inst. Sci.*, 1914, 1, 39—46).—The Kolar goldfields on the Mysore plateau are worked to a depth of 1100 m., and the rock consists of schists of very uniform character. The rocks were fused with potassium hydroxide in a copper flask under reduced pressure, and the radium emanation found to be liberated as completely as at the higher temperature required for fusion with alkali carbonates. Some nearly pure hydrogen is liberated, which causes the readings in the electroscope to be low, and it was eliminated by passing the gas over red-hot copper oxide before introducing it into the electroscope. The mean quantity of radium in the schists was found to be  $0.19 \times 10^{-12}$  gram of radium per gram of rock, the quantity varying but little with depth. These rocks, which are

probably the oldest known, contain as little radium as any yet examined, and the temperature gradient in the mines is abnormally small. Other specimens of rocks of later date contained larger amounts of radium, from 0.8 to 6.9. F. S.

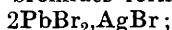
**Radioactivity and Life.** H. ZWAARDEMAKER (*Arch. Néerland. Physiol.*, 1920, **4**, 177—196).—A general discussion of work already published (compare A., 1917, i, 241; 1918, i, 326; ii, 182). W. G.

**The Cathode Fall. I. In Neon and Helium.** H. E. WATSON and G. R. PARANJPÉ (*J. Ind. Inst. Sci.*, 1918, **2**, 143—165).—From Aston's results (*Proc. Roy. Soc.*, 1911, **84**, 526), the cathode fall should be equal to the total difference of potential across the electrodes when the anode is situated in the negative glow. A systematic investigation has been made of the requirements necessary to obtain trustworthy results by this method. Using a cylindrical tube with plane parallel electrodes 7.2 cm. in diameter, the same diameter as the tube, the minimum cathode fall was found to be constant to 1 volt over a wide range of pressure—185 volts between 6 and 16 mm. for copper electrodes in neon—while the current was passing. The laws governing the relations between the cathode fall, the gas pressure, and the current were found to agree with those found by other observers using exploring wires. The cathode fall was determined in very pure helium and neon for twenty-four different metals as cathodes, and with few exceptions were all within 5% of 145.5 volts for neon and 155.5 for helium. F. S.

**The Cathode Fall. II. In Argon, Hydrogen, and Nitrogen.** GOPAL PARANJPÉ (*J. Ind. Inst. Sci.*, 1918, **2**, 166—177).—The cathode fall for twenty different metals in argon, nitrogen, and hydrogen has been determined, and in any one gas found to be nearly, but not exactly, the same for all metals. The differences in different gases for the same metal were nearly all independent of the metal, but the results in hydrogen were irregular. Nitrogen behaved very similarly to the monatomic gases. F. S.

**Electrical Conductivity in Solid Crystallised Compounds. I. Verification of Faraday's Law in the Electrolysis of Solid Salts of Heavy Metals.** C. TUBANDT and SOPHIE EGGERT (*Zeitsch. anorg. Chem.*, 1920, **110**, 196—236).—One of the most important difficulties encountered in the practical determination of the conductivity of solid salts and the verification of Faraday's law for such conductors is the short-circuiting brought about by the formation of a bridge of metal, formed by the electrolysis of the salt, between the anode and the cathode. The metal is deposited in the form of very fine threads or delicate, dendritic growths, which spread so rapidly across the electrodes that a

quantitative investigation of the electrolysis of the salt is impossible. It has been found that the cubic form of silver iodide, when electrolysed, using a silver anode and a platinum cathode, gives a deposit of silver at the cathode in the form of a perfectly coherent tree, the growth of which is so slow that there is no danger of short-circuiting. The hexagonal modification of silver iodide, stable below  $144.6^{\circ}$ , has a maximum specific conductivity of 0.00034, whilst the cubic modification has at the transition point the much greater value 1.31, which rises to 2.64 in the neighbourhood of the melting point,  $552^{\circ}$ . By carrying out the electrolysis of the salt at about  $150^{\circ}$ , using a current of 0.04 to 0.1 amp., a complete verification of Faraday's law was obtained, both the loss of silver from the anode and the weight deposited at the cathode agreeing within a fraction of 1% with the weight of silver deposited in a silver voltameter included in the circuit. The law was also verified for silver bromide, chloride, and nitrate by interposing a layer of silver iodide between the cathode and the salt under examination, the iodide ensuring that the metal was deposited at the cathode in a coherent form. The electrolysis of lead chloride, bromide, and iodide was also investigated, using a silver anode and a platinum cathode. The loss of silver from the anode afforded a complete verification of the law, but owing to the dendritic form in which the lead was deposited at the cathode, no trustworthy results could be obtained from this side. In choosing the temperature at which to carry out the electrolysis, care had to be taken that no fusion occurred, and for this purpose the fusion diagrams for the systems  $\text{PbCl}_2\text{-AgCl}$ ,  $\text{PbBr}_2\text{-AgBr}$ , and  $\text{PbI}_2\text{-AgI}$  were investigated experimentally. Silver and lead chlorides form a eutectic at  $314^{\circ}$ , containing 40 mols. % of lead chloride. Silver and lead bromides form a compound,



there are two eutectic points, the first at  $276^{\circ}$  with 46 mols. % of  $\text{PbBr}_2$ , this eutectic crystallising from mixtures containing 0—66.67 mols. % of  $\text{PbBr}_2$ , all other mixtures showing eutectic crystallisation at  $295^{\circ}$ . Silver iodide-lead iodide mixtures show eutectic crystallisation at  $395^{\circ}$  with 0—20 mols. %  $\text{AgI}$ . From this point up to 100%  $\text{AgI}$ , mixed crystals of the compound  $4\text{AgI}\cdot\text{PbI}_2$  with  $\text{PbI}_2$  are formed, the lowest crystallising point being  $344^{\circ}$ . Experiments on the electrolysis of cuprous iodide were inconclusive, on account of the difficulty of preparing the compound in a satisfactorily pure condition. E. H. R.

**Photochemical Cell with Complex Cyanides.** S. IMORI (*J. Tokyo Chem. Soc.*, 1918, **39**, 1—13).—Platinum electrodes are immersed in solutions of complex cyanides (potassium nickel or potassium platinum), and one of the electrodes is exposed to light. This electrode becomes positive, whilst it became negative in the potassium ferrocyanide cells previously examined by the author. The current quickly decays when the circuit is closed through a high resistance. The author is of opinion that the *E.M.F.* pro-

duced with these complex cyanides is not of the same nature as that obtained in other solutions. CHEMICAL ABSTRACTS.

**Electromotive Force of Alloys of Zinc and Cadmium with Tin, Lead, and Bismuth.** PAUL FUCHS (*Zeitsch. anorg. Chem.*, 1919, 109, 80—88).—The *E.M.F.* of elements composed of alloys of cadmium with tin, lead, and bismuth of various compositions as one electrode, cadmium sulphate solution and cadmium as the other electrode: alloy  $|N\text{-CdSO}_4| \text{Cd}$ , have been measured; similar cells of the type: alloy  $|N\text{-ZnSO}_4| \text{Zn}$ , in which zinc takes the place of cadmium in the alloy, have also been measured. The cells were measured in the presence of hydrogen, and only gave constant values after several days. The results confirm the views of Tammann (A., 1919, ii, 398) that the *E.M.F.* varies with the composition of the alloy only so long as one phase is present, that is, as long as the alloy is a solution or a single series of mixed crystals, but as soon as two phases appear, the *E.M.F.* is no longer dependent on the composition. J. F. S.

**The Free Energy of Potassium Hydroxide in Aqueous Solution and the Activities of its Ions.** MING CHOW (*J. Amer. Chem. Soc.*, 1920, 42, 488—497).—Experiments were made to determine, by means of electromotive force measurements, the free energy attending the transfer of potassium hydroxide in aqueous solution from one concentration to another, and from the free energy decreases to derive the relative activities of the ions of the base and its activity coefficients at various concentrations (compare MacInnes and Parker, A., 1915, ii, 510, on the free energy of potassium chloride, and Ellis, A., 1916, ii, 369, and Noyes and Ellis, A., 1918, ii, 27, on hydrochloric acid). The cells studied were of the type  $\text{Hg} + \text{HgO} - \text{KOH}(c_1) - \text{K}$  in  $\text{Hg} - \text{KOH}(c_2) - \text{Hg} + \text{HgO}$  at  $25^\circ$ . The potassium amalgam was used in the form of a dropping electrode, and potassium hydroxide concentrations were varied between 0.003 and 0.84*N*. As found by Ellis in the case of hydrochloric acid, the activity coefficient at first decreases with increasing concentration. It passes through a minimum at about 0.5 molal concentration, then increases rapidly. Up to concentrations of 0.5 molal, the activity coefficient has a much smaller value than the conductance-viscosity ratio, showing that this ratio, even at moderate concentrations, is not even an approximate measure of the effective ionisation of highly ionised substances. E. H. R.

**The Activities of the Ions in Solutions of Mixed Electrolytes.** MING CHOW (*J. Amer. Chem. Soc.*, 1920, 42, 497—502).—Determinations of the activity coefficients in mixed solutions of hydrochloric acid and potassium chloride were made from measurements of the electromotive force of cells of the type  $\text{H}_2(1 \text{ atm.}) - \text{HCl}(c_1) + \text{KCl}(c_2) - \text{Hg}_2\text{Cl}_2 + \text{Hg}$ , in which the separate concentrations  $c_1$  and  $c_2$  were varied, but their sum was kept constant at 0.1*N*. The results show that the activity

coefficient of the hydrochloric acid has substantially the same value in all the mixtures, and lend support to the view that the activity of the chlorine ion in solutions of different highly ionised univalent chlorides or of mixtures of them is determined by its own concentration, and is independent of the cations associated with it. The experimental results do not agree with those obtained by Loomis, Essex, and Meacham (A., 1917, ii, 353) from *E.M.F.* measurements of the same type of cell. E. H. R.

**The Theory of Electrolytic Ions. XIII. Conductivity of Multivalent Electrolytes.** RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1919, 109, 63—68. Compare A., 1919, ii, 262).—A correction and extension of the theoretical conceptions, on the step-wise ionisation and the degree of dissociation, put forward previously (*loc. cit.*). J. F. S.

**The Phenomena of Electrolytic Migration. Electrolysis of Mixed Solutions of Alkali Salts.** MARC H. VAN LAER (*Rec. trav. chim.*, 1920, 39, 301—329).—In the electrolysis of a normal solution of sodium hydroxide at 18°, the yield from the current is only 17·5% of that indicated by Faraday's law, but this yield is often varied by the superposition of different factors; thus, according to the direction in which they act, the hydrostatic pressure, diffusion, and electrical osmosis may favour the migration of certain ions and retard that of the ions of opposite sign. Other intervening factors are temperature, the intensity of the current, and the nature of the diaphragm between the anode and cathode liquids. Thus, in the electrolysis of a solution of sodium hydroxide, rise in temperature and cataphoresis both exert a favourable influence. On the other hand, the diffusion of the sodium hydroxide produces a loss, which increases with the concentration of the cathode liquid. As the concentration of the current,  $I/V$ , diminishes, the yield first increases gradually until it reaches a maximum and then decreases.

The electrolysis of a solution of sodium carbonate presents the same fundamental characteristics as in the case of sodium hydroxide, but in this case, as the electrolysis proceeds, the resistance of the cell increases, owing to the formation of sodium hydrogen carbonate, the carbon dioxide liberated at the anode being entirely absorbed by the solution at the ordinary temperature if the current intensity is not too great. The introduction into the solution of an oxy-salt, such as the sulphate, chlorate, or nitrate of sodium with a common cation, prevents the formation of sodium hydrogen carbonate, and thus a cathode liquid very rich in sodium hydroxide can be obtained. The nitrate gives the best result, and the yield from the current increases with the concentration of the oxy-salt.

Applying this method to barium carbonate in the presence of barium nitrate, the solid carbonate being introduced into the anode vessel, crystalline barium hydroxide was readily obtained.

W. G.

**Diamagnetism of Odorous Substances.** H. ZWAARDEMAKER and F. HOGEWIND (*Arch. Néerland. Physiol.*, 1920, **4**, 224—232).—The authors have measured the diamagnetism of a large number of odorous substances, and plotting the values found against the number of atoms in the molecule, it is found that, for an homologous series, the points lie on practically a straight line, but that the differences between the values obtained for adjacent members in a series vary from series to series. W. G.

**A Method for Determining the Relationship between the Melting Point of a Crystal Lamella and its Thickness.** G. TAMMANN (*Zeitsch. anorg. Chem.*, 1920, **110**, 166—168).—The method suggested is to form by crystallisation a lamella of variable thickness between a plate and a cylindrical lens, and to have in the metal plate a temperature gradient so that the contact line between the plate and the lens is perpendicular to the isotherms in the plate. If the melting point lies between the temperatures of the two ends of the plate, part of the substance melts, and the bounding curve between the liquid and crystalline portions shows by its form the influence of the thickness of the lamella on the melting point. The work required to disrupt the crystal is inversely proportional to the thickness of the lamella, and it follows that the influence of the lamella thickness on the melting point is also inversely proportional to the lamella thickness. Thermodynamically, it is shown that the work required is equal to the change of equilibrium temperature multiplied by the entropy of unit mass at the melting point. E. H. R.

**The Influence of State of Division on Melting Point.** F. MEISSNER (*Zeitsch. anorg. Chem.*, 1920, **110**, 169—186).—The conclusions of Pavlov (*A.*, 1909, ii, 19, 295, 800: 1910, i, 740) regarding the influence of size of particles on melting point are adversely criticised. The growth of large crystals at the expense of small ones is to be attributed, not to difference of vapour pressure between large and small crystals, but to fluctuations in temperature. Pavlov's observation that small particles of salol, 8 to 15  $\mu$  in diameter, melt several degrees below the normal melting point, could not be confirmed.

The only satisfactory method of examining the relation between state of division and melting point is by the investigation of thin lamellæ, formed by allowing a molten substance to crystallise between two plates. Such lamellæ admit of theoretical treatment, in which the surface energy of the crystal can be considered in the same manner as that of a liquid. If  $A_0 - A'_0$  be the difference between the surface energies of crystal and liquid, the following relation holds:  $A_0 - A'_0 = (T_1 - T_0)/T_0 \cdot RQ/2 \cdot d \cdot d_0/(d_1 - d_2)$ , where  $T_0$  is the normal melting point,  $T_1$  and  $T_0$  the fusion temperatures of lamellæ of thickness  $d_1$  and  $d_2$  respectively,  $R$  the latent heat of fusion, and  $Q$  the density of the fused substance. To determine the value of  $A_0 - A'_0$ , it is necessary to know the relation between melting point and lamella thickness. The experimental method



used was that suggested by Tammann (preceding abstract), in which wedge-shaped lamellæ were formed between a cylindrical lens and a metal plate having a uniform temperature gradient from end to end. In the cases of azobenzene, tristearin, and myristic acid, the boundary curves formed between solid and liquid were distinctly displaced towards the cold end of the plate as the thickness of the lamella diminished. In the case of azobenzene, the displacement represented a difference of  $0.355^{\circ}$  in the melting point for a change of thickness from  $0.8$  to  $10\mu$ . In the case of tristearin, the temperature difference was  $0.199^{\circ}$ , and for myristic acid  $0.258^{\circ}$ . The surface energy differences between crystal and liquid, calculated from the above equation, were in the three cases 67, 50, and 59 ergs respectively. In a number of other cases, including salol, acetamide, and glauber salt, the temperature difference was of the same order as in the case of myristic acid, whilst with *p*-chloroaniline and stearic acid, no difference due to diminishing thickness of the lamella could be detected.

E. H. R.

**Phenomena Observed during the Melting, Freezing, and Boiling of Mixtures of Ammonium Chloride and other Chlorides.** KURT HACHMEISTER (*Zeitsch. anorg. Chem.*, 1919, 109, 145—186).—Cooling curves have been constructed for ammonium chloride, cuprous chloride, lithium chloride, zinc chloride, cadmium chloride, ferric chloride, thallous chloride, and lead chloride, and for mixtures of ammonium chloride with cuprous chloride, lithium chloride, zinc chloride, cadmium chloride, ferric chloride, thallous chloride, and lead chloride. Very complete diagrams of condition are constructed for the binary mixtures. In connexion with the simple salts, much of the data obtained differs from that previously published. The transition point of ammonium chloride is found to be  $174^{\circ}$  (Wegscheider, A., 1918, ii, 298,  $184.5^{\circ}$ ). The following melting points are obtained: cuprous chloride,  $425^{\circ}$ ; lithium chloride,  $605^{\circ}$ ; zinc chloride,  $283^{\circ}$ ; cadmium chloride,  $568^{\circ}$  (b. p.  $964^{\circ}$ ); ferric chloride,  $303^{\circ}$ ; thallous chloride,  $427^{\circ}$ ; lead chloride,  $501^{\circ}$ . It is shown that by mixing other chlorides with ammonium chloride, this substance may be obtained molten. The compounds  $\text{CdCl}_2\cdot\text{NH}_4\text{Cl}$ ,  $2\text{ZnCl}_2\cdot\text{NH}_4\text{Cl}$ , and  $\text{FeCl}_3\cdot\text{NH}_4\text{Cl}$ , in addition to the double compounds already known, are indicated by the temperature composition diagrams. In the binary mixtures of ammonium chloride with cuprous chloride and lithium chloride, respectively, simple eutectics are formed, but no compounds. The compound formed between equimolecular quantities of ferric chloride and ammonium chloride is peculiar in possessing a definite boiling point,  $386^{\circ}$ . Mixtures of ammonium chloride with lead chloride and thallous chloride, respectively, cannot be melted. Ammonium chloride shows great similarity in its behaviour with other chlorides to the alkali chlorides. The nearer the two chlorides are in general properties, the simpler is the binary system formed between them.

J. F. S.

**Melting Points of the Members of Homologous Series.**

G. TAMMANN (*Zeitsch. anorg. Chem.*, 1919, **109**, 221—225).—A theoretical paper in which regular rise and fall of the melting point of members of the monocarboxylic aliphatic acids is discussed. It is suggested that the acids with an even number of carbon atoms exist in two stable, crystalline forms, and that this furnishes the reason for the course of the melting points in this series. In support of this hypothesis, it is shown that acetic acid exists in two such forms, the triple point of which lies at  $57.5^{\circ}$  under a pressure of 2330 kilos. per sq. cm. No such isomerides have been observed for the acid with an uneven number of carbon atoms, formic acid. J. F. S.

**Critical Data and Chemical Constitution.** W. HERZ

(*Zeitsch. anorg. Chem.*, 1919, **109**, 293—296).—A theoretical paper in which the author has tabulated the critical pressure and critical temperature of a large number of members of the following homologous series: paraffins (9), olefines (3), methyl esters of the monocarboxylic aliphatic acids (6), ethyl esters of the same acids (6), ethers, amines (6), benzene hydrocarbons (11), aromatic amines (3), and other organic substances. It is shown that the critical temperature increases with increasing number of carbon atoms, and the critical pressure decreases with increasing number of carbon atoms. When the quotient of the critical temperature in absolute degrees and the critical pressure is divided by the number of carbon atoms, an approximate constant is obtained ( $2.5$ — $4.0$ ) for aliphatic compounds and  $1.9$ — $2.4$  for aromatic compounds. A much better constant is obtained if, instead of the number of carbon atoms, the total number of atoms is used; here the constant is  $0.99$ — $0.69$  for aliphatic compounds and  $0.98$ — $0.90$  for aromatic compounds. Further, if the quotient is divided by the total number of valencies, a very good constant is obtained,  $0.50$ — $0.41$  for aliphatic compounds and  $0.43$ — $0.37$  for aromatic compounds. J. F. S.

**New Instrument for Measuring Vapour Tension.** HAROLD

MOORE (*J. Soc. Chem. Ind.*, 1920, **39**, 78—80r).—An instrument for making rapid and accurate measurements of the vapour pressure of motor spirit is described. It consists of two tubes about  $\frac{1}{4}$  in. bore and 800 mm. long connected to each other and to a levelling bottle by means of a Y-piece and thick-walled rubber tubing. The two tubes are clamped vertically, and have mercury-sealed cocks at their upper ends, which close the tubes to small, graduated cups. One of the tubes is surrounded by a water-jacket. To make a measurement, the whole apparatus is filled with mercury, then a measured volume of spirit is admitted into one of the tubes from the small cup at the top, and the reservoir lowered. The barometric height is read from one tube, and the barometric pressure diminished by the vapour pressure of the spirit is read from the other tube. The vapour pressure of crystallisable benzene, ethyl alcohol, and petrol has been deter-

mined over the temperature range 10—50°, and also the vapour pressure of a series of mixtures of alcohol and petrol and alcohol and benzene at 20°, 30°, 40°, and 50°. Working with water, the error observed in the vapour pressure was about 3 mm., but with mixed motor spirits it will probably be much greater. J. F. S.

**The Vapour Pressures of Cadmium, Lead, and Tin Amalgams.** JOEL H. HILDEBRAND, A. H. FOSTER, and C. W. BEEBE (*J. Amer. Chem. Soc.*, 1920, **42**, 545—548).—A continuation of previous work on the vapour pressures of liquid amalgams (compare A., 1913, ii, 471, 755; 1914, ii, 800; 1916, ii, 14). The vapour pressures of mercury over amalgams of cadmium, lead, and tin were measured at 324°, by the method previously described, at intervals covering the entire range of concentrations, and the values of the constants  $a$  and  $c$  were calculated in the empirical equation  $\log p/p_0 = \log N + a/(1 + cn)^2$ , where  $n$  represents the number of molecules of mercury per molecule of the other metal,  $N = n/n + 1$ ,  $p_0$  is the vapour pressure of pure mercury, and  $p$  that of the amalgam of composition corresponding with  $n$ . Cadmium amalgams show vapour pressures less than those demanded by Raoult's law,  $p/p_0 = N$ , and the deviations can be calculated on the assumption of partial solvation, varying with the concentration according to the mass law, to form molecules of  $\text{CdHg}$ . Lead and tin amalgams give practically equal vapour pressures, which are much greater than Raoult's law demands. The deviations cannot be accounted for by the assumption of any simple molecular change. E. H. R.

**The Aqueous Pressure of some Hydrated Crystals. Oxalic Acid, Strontium Chloride, and Sodium Sulphate.** GREGORY PAUL BAXTER and JOHN ERNEST LANSING (*J. Amer. Chem. Soc.*, 1920, **42**, 419—426).—With the object of perfecting a trustworthy method of measuring the aqueous pressures of hydrated crystals, experiments were made with oxalic acid, strontium chloride, and sodium sulphate, and the following method was found to give satisfactory results. The hydrated crystals were intimately mixed with 5—10% by weight of the dehydrated substance, and the mixture was packed, interspersed with glass beads, in a large U-tube. The method of experiment was to pass a measured volume of dry air through the column of crystals at constant temperature, subsequently passing the air through weighed drying tubes containing phosphoric oxide. The curves obtained by plotting the logarithm of the vapour pressure found against the reciprocal of the absolute temperature were very nearly straight lines, almost exactly so in the case of sodium sulphate crystals. E. H. R.

**The Vapour Pressures of Concentrated Solutions.** G. R. PARANJPE (*J. Ind. Inst. Sci.*, 1918, **2**, 59—72).—Measurements were made between 0° and 40° of the vapour pressures of solu-

tions of (1) potassium hydroxide for concentrations between 18.81 and 138.2 grams of the anhydrous hydroxide in 100 grams of water; (2) sodium hydroxide for concentrations between 14.62 and 113.1 grams in 100 grams of water; (3) calcium chloride for concentrations between 14.81 and 119.5 grams of the anhydrous salt in 100 grams of water. The results obtained for potassium hydroxide are not in very close agreement with those obtained by Dieterici (compare A., 1891, 783; 1898, ii, 207; 1899, ii, 403).

W. G.

**Determination of Boiling Point.** SCHIMMEL & Co. (*Bericht*. April-October, 1919, 100—102; from *Chem. Zentr.*, 1920, ii, 422—423).—In connexion with the apparatus described recently by Paul and Schautz (A., 1919, ii, 422), the authors recommend the adoption of definite normal pressures for data concerning boiling points, particularly for such as are determined in a vacuum. As absolute unit of pressure, the bar (one dyne per sq. cm.) is advocated. One atmosphere = 1,013,200 bars, or 10 kilobars correspond fairly closely with 75 mm. Measurements should be effected at normal pressures, a simple type of apparatus for the measurement of the latter being depicted in the original. Measurement of pressure in vacuum distillation (particularly in a high vacuum) is only accurate when it is effected close to the point at which the temperature is observed. The errors in the older method, in which the manometer is attached to the exhaust pipe, increase with increase of the vacuum and the velocity of distillation, with the decreasing width of distillation and condensing tubes, and with leaks in the apparatus.

H. W.

**Physical Behaviour of Liquids.** W. HERZ (*Zeitsch. Elektrochem.*, 1920, 26, 109—111).—A theoretical paper in which formulæ are developed whereby the molecular boiling-point elevation and the capillarity constant at the boiling point may be calculated from the critical data. These formulæ have the form: (1)  $c = 4T_k^2 d_k / 3p_k$ ; (2)  $a = 0.03643 p_k / d_k$ , in which  $p_k$  is the critical pressure,  $T_k$  the critical temperature,  $d_k$  the critical density,  $c$  is the molecular elevation constant, and  $a$  the Poisson capillarity constant. A further formula for calculating the vapour pressure is also developed; this has the form

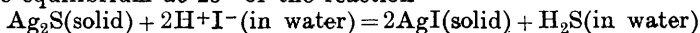
$$\log(p_s/p_1) = 4.91(T_s/T_1 - 1),$$

in which  $p_s$  is the vapour pressure at the boiling point  $T_s$ , and  $p_1$  the vapour pressure at the temperature  $T_1$ . The values obtained by the use of these formulæ have been compared with the experimental values, and found in the case of non-associated liquids, both organic and inorganic, to be in good agreement.

J. F. S.

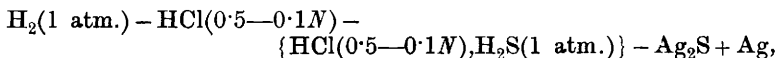
**Vapour Tension and Heat of Vaporisation, and the Dependence of the Factors  $\alpha$  and  $b$  on the Temperature and the Volume.** J. J. VAN LAAR (*Rec. trav. chim.*, 1920, 39, 215—242).—A mathematical discussion of the subject. W. G.

**A Thermodynamic Investigation of Reactions Involving Silver Sulphide and Silver Iodide.** ARTHUR A. NOYES and E. STANLEY FREED (*J. Amer. Chem. Soc.*, 1920, **42**, 476—487).—The equilibrium at 25° of the reaction

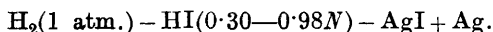


was studied with the object of determining how the activity coefficient (or effective ionisation) of the acid varies with its concentration, and to determine the free energy change attending the reaction. The concentration of hydriodic acid was necessarily confined within the limits 0.024 to 0.116*N*. The equilibrium constant, *K*, calculated from the formula  $K = C_{\text{H}_2\text{S}}/(C_{\text{HI}}\gamma)^2$ , where  $\gamma$  is the ionisation constant, has a mean value 964. Assuming that the activity coefficient at  $C_{\text{HI}} = 0.025N$  is identical with the ionisation constant, it is found that between concentrations 0.025 and 0.12 the activity coefficient decreases 4.5%, compared with 8.3% found by Noyes and Ellis for hydrochloric acid (*A.*, 1918, ii, 27).

*E.M.F.* measurements were made between 5° and 25° of the cells



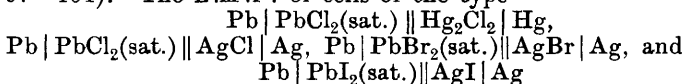
and at 25° of the cells



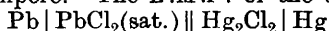
From the data obtained, a number of free energy calculations are made, and are compared with the results of calculations made using data from other sources. Finally, the following figures are adopted: for the free-energy decrease attending the reaction  $2\text{AgI} + \text{H}_2(1 \text{ atm.}) = 2\text{Ag} + 2\text{H}^+ + 2\text{I}^-$  at 25°, -6885 cal., and for the reaction  $\text{Ag}_2\text{S} + \text{H}_2(1 \text{ atm.}) = 2\text{Ag} + \text{H}_2\text{S}(1 \text{ atm.})$  at 25°, -1485 cal. Making use of the value found for the free energy of formation of iodide ion by Lewis and Randall (*A.*, 1914, ii, 840), the free-energy value for the reaction  $2\text{Ag} + \text{I}_2 = 2\text{AgI}$  is found to be +31,493 cal. Half this quantity is the free-energy decrease attending the formation of one molecule of solid silver iodide from its elements at 25°.

E. H. R.

**Use of Lead Electrodes for Thermochemical Measurements.** CONSTANZE KRAHMER (*Zeitsch. Elektrochem.*, 1920, **26**, 97—104).—The *E.M.F.* of cells of the type

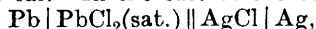


has been measured at a number of temperatures, and from the data thus obtained the heat of formation of lead chloride, silver bromide, and silver iodide has been calculated. The lead electrodes were prepared on platinum wire by electrolysis a solution of 8% hydrofluosilic acid and 4% lead silicofluoride by means of a current of 0.001 ampere. The *E.M.F.* of the cell



is given by the formula  $E_{293} = 0.53113 - 0.000191(20 - t)$ , and the

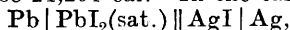
heat of the reaction  $\frac{1}{2}\text{Pb} + \text{HgCl} = \frac{1}{2}\text{PbCl}_2 + \text{Hg}$  is  $U_{293} = 10,949 \pm 0.1\%$  cal., from which the heat of formation of lead chloride is calculated to 85,521 cal. In the case of the cell



$E_{293} = 0.49328 + 0.000125(t - 20)$ ,  $U_{293} = 12,211 \pm 24$  cal., and assuming the heat of formation of silver chloride to be 30,505 cal., the heat of formation of lead chloride is 85,432 cal. The *E.M.F.* of the cell  $\text{Pb} | \text{PbBr}_2(\text{sat.}) || \text{AgBr} | \text{Ag}$  is

$$E_{293} = 0.35252 + 0.000126(20 - t^\circ)$$

and  $U_{293} = 8974 \pm 44$  cal.; using the value 66,350 cal. for the heat of formation of lead bromide, the heat of formation of silver bromide is found to be 24,201 cal. In the case of the cell



$E_{293} = 0.21205 + 0.000129(20 - t)$  and  $U_{293} = 5758 \pm 57$  cal., and the heat of formation of silver iodide is 15,192 cal. When the haloids used were crystalline, slightly different values are found for the above-named cells. A number of experiments with evacuated elements show that the gradual falling of the *E.M.F.* of the cell  $\text{Pb} | \text{PbCl}_2(\text{sat.}) || \text{Hg}_2\text{Cl}_2 | \text{Hg}$  is not due to oxidation, but is in some way connected with the size of the lead crystals. A table of comparison of the present values with those of Thomsen, Berthelot, and other observers is included in the paper. J. F. S.

**Heat of Solution.** G. TAMMANN (*Zeitsch. anorg. Chem.*, 1920, 109, 215—220).—A theoretical paper in which it is shown that from a knowledge of the heat of solution of one substance in another, it is possible to decide whether or no a chemical reaction has taken place during solution. The heat of solution is made up of heat quantities brought about by (i) the conversion of an anisotropic substance into an isotropic condition, (ii) the mixture of the isotropic substance with the solvent, and (iii) chemical processes, such as formation of compounds, change in molecular weight, and ionisations. The dimensions of the first two quantities can be calculated theoretically, hence from the experimentally determined heat of solution it is possible to see whether any heat change due to the third cause is contained in the experimental value, and so ascertain whether chemical processes have taken place. J. F. S.

### Heat of Solution and the Partial Molal Heat Content of the Constituents in Aqueous Solutions of Sodium Chloride.

MERLE RANDALL and CHARLES S. BISSON (*J. Amer. Chem. Soc.*, 1920, 42, 347—367).—The partial molal heat content of a substance is its heat content when in solution at a given concentration, and is defined as the increase in the heat content of a large amount of the solution at the given concentration when one mol.

of the substance is added to it. The symbol  $\bar{H}$  is used for this quantity, and  $H$  for the absolute molal heat content of the substance. It follows that the partial molal heat of solution of a substance, for example, sodium chloride, is given by  $\bar{H}_c - H_{\text{NaCl}}$

for a concentration  $c$ . The symbol  $\Delta H$  is used to represent the partial molal heat content of a substance formed from its elements in their standard state at the same temperature. The specific heats of sodium chloride and potassium chloride solutions were first determined for different concentrations at  $25^\circ$ . The partial molal heat of solution of water in sodium chloride solution,  $H - H_{H_2O}$ , was determined by measuring the heat absorbed per mol. of water when water was added to sodium chloride solutions of known concentrations. Starting with saturated sodium chloride solutions, the values rise gradually from about 11 cal. at  $6.25M$  to 21 cal. at  $4.2M$ , and then gradually diminish to zero at infinite dilution.

The heat of dilution of sodium chloride was also measured calorimetrically by adding small amounts of saturated solution to a large volume of water. The value found at infinite dilution was 606 cal. The mean heat of solution of sodium chloride in a very large amount of water was found experimentally to be 1019 cal. From the values obtained, the partial molal heat content of sodium chloride,  $\Delta H$ , at  $25^\circ$  in solution at all concentrations was calculated. The value of  $\Delta H$  increases from  $-96,781$  at infinite dilution to  $-97,500$  in a saturated solution, whilst the partial molal heat content of the water decreases from  $-68,272$  at infinite dilution to  $-68,250$  at  $4.2M$ , increasing again to  $-68,261$  in a saturated solution.

E. H. R.

**Chemical Affinity. XII. Thermodynamical Relationship between the Mixture Affinities of Partially Saturated Solutions and its Application to the Estimation of Affinity.**

J. N. BRÖNSTED (*K. Danske. Vidensk. Medd. Math. Phys.*, 1918, 1, No. 5, 1—39; from *Chem. Zentr.*, 1920, i, 404—405. Compare this vol., ii, 298).—A relationship has been established between the mixture potentials of two components in a mixture in which the potential of the other substances present is maintained constant, as, for example, by invariably using solutions saturated with these substances. The relationship may be expressed by the equation  $x \cdot dA_1/dx + (1-x)dA_2/dx = 0$  or  $n_1 dA_1 + n_2 dA_2 = 0$ , in which  $A_1$  and  $A_2$  are the molecular differential mixture potentials of the components, and  $n_1$  and  $n_2$  the number of molecules in the mixture. The equation has therefore the same form as if the two components are present in binary mixtures. The theory is developed for the formation of double salts, for allotropic transformation, and for reciprocal pairs of salts, and is applied in particular to the cases of  $\alpha$ - and  $\beta$ - $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  and of carnallite and schönite. The affinity of the reactions  $\text{KCl} + \text{NaClO}_3 \rightarrow \text{KClO}_3 + \text{NaCl}$  and  $\text{KCl} + \text{NaNO}_3 \rightarrow \text{KNO}_3 + \text{NaCl}$  has been measured at  $16.39^\circ$  by estimation of the vapour pressure; the values 2020 cal. and 740 cal. are obtained, which agree closely with the data previously deduced from electrometric measurements, and thus afford a sharp verification of the theory. An experimental method is also described which permits the simultaneous estimation of

vapour tension and concentration of solutions, and also indicates in a simple manner the points at which saturation in respect to one or two components occurs.

H. W.

### **A Surface Tensimeter for Small Quantities of Liquids.**

C. C. KIPLINGER (*J. Amer. Chem. Soc.*, 1920, **42**, 472—476).—A method has been devised by means of which the surface tension of a liquid may be determined when only a drop or two is available. A capillary glass tube, about 18 cm. long, 1 mm. internal and 4 mm. external diameter, is carefully made with its ends, as nearly as possible, plane and accurately rectangular with the length. By means of a special device (A., 1918, ii, 360), the tube can be attached to a quadrant cut from a celluloid protractor. A small notch cut in the apex of the quadrant holds in position a thread, which passes over it, the thread carrying a small weight at each end and serving to indicate the angular displacement of the tube. The apparatus is held in position by a suitable clamp on a stand. A short column of the liquid to be examined is introduced into the clean, dry capillary tube, and the tube is turned through such an angle that the meniscus at the lower end changes to a plane surface. The point at which this occurs is observed by means of a pocket lens, and the angular displacement from the vertical is read off on the quadrant. The length,  $l$ , of the column is measured to 0.1 mm., and from the equation  $l \cos A = h$ , the height,  $h$ , of the vertical column exerting the same pressure as the inclined column of liquid is calculated. The surface tension is then calculated from the usual formula,  $T = d \times h \times r \times 980/2$  dynes per cm. The results obtained are generally 2—4% low. The method may be used to assist in identifying organic liquids.

E. H. R.

### **Adsorptive Power of Different Forms of Charcoal.**

K. SCHERINGA (*Pharm. Weekblad*, 1920, **57**, 348—350).—The most adsorptive charcoal was obtained by heating the material to be charred to a high temperature. Low-temperature carbonisation of filter paper, or previous impregnation of the material with sodium chloride, gave an inferior adsorbent.

W. S. M.

**Some Aspects of the Behaviour of Charcoal with respect to Chlorine.** G. S. BOHART and E. Q. ADAMS (*J. Amer. Chem. Soc.*, 1920, **42**, 523—544).—Experiments on the absorption of chlorine by charcoal showed considerable variations in the behaviour of single samples, which could only be attributed to differences in the humidity of the current of chlorine-laden gas. A series of experiments was therefore carried out on the effect of moisture and, in addition, the influence of variations in temperature and pressure, of the velocity of the gas through the charcoal and of the density of the charcoal and the depth of the absorbing layer, were studied. Two processes take place during the passage of the gas through the charcoal, absorption or adsorption, which cannot be distinguished, and catalytic formation of hydrochloric acid. The results of the



experiments are illustrated by means of curves, in which the percentage of chlorine or hydrochloric acid transmitted is plotted against time. The period during which no chlorine or hydrochloric acid is transmitted is called the service time of the charcoal. The service times of different charcoals could not be correlated with their apparent density. For any one sample of charcoal, the service time increases more rapidly than the thickness of the absorbing layer. Charcoals with the greatest chlorine capacity were found to be the best catalysts for the reaction between water and chlorine. The effect of humidity was studied by varying the moisture content of the gas stream, air to chlorine in the ratio 500:1, from 0—80% saturation at 25°. Hydrogen chloride always appeared in the transmitted gases before chlorine, and when chlorine appeared as well, the effect of the moisture could be seen, particularly in the 80% saturation experiment, in the greater proportion of acid to free chlorine. The duration of complete chlorine absorption passes through a minimum at about 50% saturation. Below 12.5°, chlorine appeared in the gases before hydrogen chloride; above this temperature, the reverse was the case. The service time is at a minimum between 0° and 12.5°. Reductions in pressure have little, if any, effect. The chlorine capacity of the charcoal is increased by one exposure to chlorine, followed by heating to dull redness in a vacuum. E. H. R.

**The Velocity of Adsorption of Chloropicrin and Carbon Tetrachloride by Charcoal.** HERBERT S. HARNED (*J. Amer. Chem. Soc.*, 1920, **42**, 372—391).—The experiments recorded were carried out for the purpose, first, of obtaining reproducible results in the measurements of the velocity of adsorption of gases on a relatively gas-free solid surface, and, secondly, of determining the effect of a foreign gas on this velocity. The method of experiment adopted was to expose the charcoal for a measured time to the vapour to be adsorbed at a low pressure (the vapour pressure of the compound), and to determine the amount of adsorption by the increase in weight of the charcoal. Charcoal was chosen for examination on account of its exceedingly large adsorbing surface, and chloropicrin and carbon tetrachloride as gases on account of their relatively high molecular weight, and the consequently relatively considerable weight of gas adsorbed. The results are shown by series of curves, in which the weight of gas adsorbed per gram of charcoal is plotted against time. In no case could reproducible results be obtained until the charcoal had been heated to more than 700° in a vacuum, cooled in a vacuum, exposed to the gas until a considerable quantity was adsorbed, and again heated above 700° in a high vacuum. This process of washing out with the gas under examination is necessary to remove foreign gases, which cause an initial lag in the adsorption. When the charcoal is in such a condition that the maximum velocity of adsorption is attained, the process follows the equation

$$m = 1/t \cdot \log A / A - K,$$

where  $K$  is the amount adsorbed per gram of charcoal in time  $t$  and  $A$  is the amount adsorbed when  $t$  is infinite,  $m$  being a constant. The curve obtained by plotting  $\log A/A - K$  against  $t$  is then a straight line. The results are in agreement with Langmuir's theory of adsorption (A., 1918, ii, 430), in which he assumes that the adsorbed layer of gas is only one molecule deep. Some of the results for carbon tetrachloride indicate the possibility of the formation to a certain extent of a second adsorbed layer, but the influence of small quantities of foreign gases on the rate of adsorption may account for the divergence of the curves, in these cases, from straight lines. E. H. R.

**Evaluation of Dissociation Measurements of [Metal] Ammines by means of the Nernst Theorem and Nomograms.** WILHELM BILTZ and GUSTAV F. HÜTTIG (*Zeitsch. anorg. Chem.*, 1919, 109, 111—125. Compare this vol., ii, 318).—A theoretical paper in which the method of evaluating and comparing dissociation pressures of ammines is described. The heat of dissociation at the absolute zero ( $Q_0$ ) and the coefficient of  $T$  are determined from the Nernst equation  $\log p = -Q_0/4.57T + 1.75 \log T + (\sum \nu \beta + \sum n b)/4.57 \cdot T + 3.3$ . Nomograms are given by means of which the calculations, both for the complete and the approximate Nernst formula, are replaced by readings from scales. The value of  $Q_0$  is shown to be constant in the case of the ammines of iron, cobalt, nickel, and manganese, and is in agreement with the calorimetric values and those calculated according to the van't Hoff rule. The coefficient of  $T$  is, within the limits of experimental error, in keeping with the thermochemical data; it is independent of the nature of the ammonia-free salt, but depends on the nature of the linking of the combined ammonia. The combined ammonia has a larger molecular heat in the hexammines than in those compounds with less ammonia. The dissociation temperature of all the ammines is determined by the nomograph for  $p=100$  mm. The values are compared with those obtained by a graphic approximation method, and the two sets of values shown to be in moderate agreement. The nomographic method is superior to the graphic method, and also more convenient in use. J. F. S.

**Nomographs from the Functions  $\log p = -Q/4.57T + 1.75 \log T + C$  and  $\log p = -Q/4.57T + 1.75 \log T - aT + 3.3$ .** H. von SANDEN (*Zeitsch. anorg. Chem.*, 1919, 109, 126—131. Compare preceding abstract).—A theoretical paper in which the method of drawing and using nomographs is described. A nomograph is a series of lines and curves by which the relationships of functions with several variables may be represented (see "Traite de Nomographie." d'Ocagne). In the case of the two functions named above, the nomograph is constructed as follows. Two vertical lines are drawn, of which the one standing to the left is graduated for pressure in millimetres of mercury; the other is divided to

give values of  $Q$ ; to the right of these lines, a series of curves are drawn, one for each value of  $C$  or  $\alpha$ , and each of these curves is subdivided to give temperature values. To illustrate the use of the nomograph thus constructed, an example will best serve. Suppose  $Q$ ,  $T$ , and  $C$  are known and the corresponding value of  $p$  is desired. The value of  $T$  on the appropriate  $C$  curve is sought out, and the point joined by a straight line with the corresponding  $Q$  value. The line is then produced, and the point where it cuts the pressure line gives the corresponding  $p$  value. J. F. S.

**Diffusion of Organic Substances in Organic Solvents and the Examination of Stokes' Formula.** ERNST DUMMER (*Zeitsch. anorg. Chem.*, 1920, 109, 31—51).—The author has determined the diffusion coefficient, the viscosity, and index of refraction of nitromethane, ethyl acetate, nitrobenzene, benzotrichloride, acetone, ethyl benzoate, and methyl alcohol, and solutions of these substances in one another. From the results, the radius of the various molecules is calculated by means of the Stokes-Einstein formula  $D = RT/N \cdot 1/6\pi\eta r$ , in which  $R = 8.32 \times 10^7$  and  $N = 6.20 \times 10^{23}$ , and these values are compared with the theoretical values. It is shown that the radius in a given case is different, depending on the molecular weight of the diffusing substance and the solvent. Certain regularities are apparent in the results; thus a smaller value is found for the radius of a given substance the larger the molecular weight of the solvent. An exception to this is found only in the calculation of the radius from the diffusion of ethyl benzoate into methyl alcohol, and from the diffusion of nitrobenzene into methyl alcohol. From the results, it can be stated generally that the Stokes-Einstein formula may only be applied to the region of molecular dimensions with the greatest caution. J. F. S.

**Solubility. I. Solubility of Salts in Solutions of Salts.** J. N. BRÖNSTED (*K. Danske. Vidensk. Medd. Math. Phys.*, 1919, 2, No. 10, 1—46; from *Chem. Zentr.*, 1920, i. 402—403).—The theory of the solubility of salts in solutions of salts is developed on the preliminary hypothesis that the coefficient of activity in a mixed salt solution is the same for every ion of the same type. The calculation of the coefficient of activity,  $f$ , is based on the observation of Noyes and Falk that the behaviour of a number of binary salts can be summarised by the expression  $2 - i = K \sqrt[3]{c}$  in which  $i$  is van't Hoff's factor,  $c$  the equivalent concentration, and  $K$  a constant which is characteristic for each salt; by the substitution of  $2a = K$ , the following equation is derived:  $\log^{10} f = -1.373a \sqrt[3]{c} = -a \sqrt[3]{c}$ . The development of the theory depends on whether the solvent and dissolved substance have a common ion or not; both cases are considered and illustrated by experimental data. The following solubilities are cited: dichlorotetramminecobalt thiocyanate in sodium chlorate solution; trans-dinitrotetramminecobalt in potassium formate solution; oxalo-

tetramminecobalt perchlorate in sodium formate solution; dichlorotetramminecobalt bromide in potassium bromide solution; *trans*-dinitrotetramminecobalt chloride in potassium chloride solution; *isothiocyano*pentamminecobalt sulphate in magnesium sulphate solution. H. W.

**Supersaturation and Crystal Size.** WILDER D. BANCROFT (*J. Physical Chem.*, 1920, **24**, 100—107).—A theoretical paper in which the theory put forward by von Weimarn in connexion with the relationship between the degree of supersaturation and the size of crystals ("Grundzüge der Dispersoidchemie," 1911, 39) is discussed and shown to be inadequate, because it does not take account of the number of nuclei formed. It is shown that, with vigorous stirring and increasing supersaturation, a substance, which normally is precipitated anhydrous, may be obtained as a colloidal solution, a curdy precipitate, fine crystals, coarse crystals, or a gelatinous precipitate. At higher temperatures, precipitates are, as a rule, more coarsely crystalline than at lower temperatures. The theory of von Weimarn applies to solutions which are not stirred. The conditions for forming large crystals are those in which there is no spontaneous formation of nuclei and in which the rate of crystallisation is so slow that branched crystals do not form. The effect of adsorption on the growth of crystals is not adequately covered by von Weimarn's theory. J. F. S.

**The Relation between Growth Forms and the Structure of Crystals.** PAUL NIGGLI (*Zeitsch. anorg. Chem.*, 1920, **110**, 55—80).—A theoretical paper in which the modern theory of crystal structure is applied to the discussion of the development of crystal forms both during the growth of a crystal and during its dissolution. The faces which attain maximum development are perpendicular to the directions of maximum velocity of growth, and these faces correspond with the principal planes in the lattice structure. The whole crystal is regarded as a polymerised co-ordinated compound; the inner atoms are saturated, but those on the surface are unsaturated in certain directions. It is shown that, since the directions in which the unsaturated valencies are active are determined by the structure of the crystal, faces with complex indices should grow with greater velocity than simpler faces, because the development of such complex faces exposes to a greater extent the free atomic valencies. To a certain depth, which can be calculated, the crystal can be regarded as imperfectly formed in the plane of these complex faces, and the greater the depth of this partly crystalline layer, the greater will be the velocity of growth of the corresponding face. Statistical calculations for different types of cubic crystals show that the theoretically most probable faces are those which indeed actually occur, for example, in crystals of sodium chloride and zinc blende. The occurrence of vicinal faces is also in accordance with the theory. E. H. R.

**Structure Distortion in Plastic Fluid Crystals.** O. LEHMANN (*Ann. Physik*, 1920, [iv], **61**, 501—532).—An account of some experiments on the optical properties of fluid crystals. Mixed fluid crystals, for example, cholesteryl chloride and propionate, when mechanically distorted between a microscope slide and cover slip, exhibit optical rotation, varying in magnitude and direction with the proportions of the two constituents present. E. H. R.

**Electrical Double Refraction of Colloids.** C. BERGHOLM and Y. BJÖRNSTÅHL (*Physikal. Zeitsch.*, 1920, **21**, 137—141).—Sols of vanadium pentoxide, gold, and silver have been examined, by means of a method employed by Brace (*Phil. Mag.*, 1904, [vi], **7**, 317), under the influence of an alternating electric field, and in every case shown to be double refracting. This implies that the particles of these sols are not spherical and do not possess spherical symmetry. The double refraction in a gold sol, the particles of which have a diameter of about  $100\ \mu\mu$ , changes with the frequency; with a potential of 400 volts per cm., the phase difference is 35% greater at 3000 periods than at 50 periods. J. F. S.

**The Gold Numbers of Protalbic and Lysalbic Acids.** ROSS AIKEN GORTNER (*J. Amer. Chem. Soc.*, 1920, **42**, 595—597).—The gold numbers of protalbic and lysalbic acids, determined by Zsigmondy's process (*A.*, 1903, i, 135), are 0.15—0.20 and 0.10—0.125 respectively. Comparison of these with those for dextrin (125—150), soluble starch (10—15), sodium oleate (2—4), egg-albumin (0.08—0.10), and gum arabic (0.10—0.125) suggests that the protective action of the acids in question has been much overrated. J. K.

**The Coagulation of Clay Suspensions and Silicic Acid.** OTTO M. SMITH (*J. Amer. Chem. Soc.*, 1920, **42**, 460—472).—The experiments recorded were made with the object of determining the action of electrolytes commonly occurring in natural waters on the stability of colloidal clay suspensions and silicic acid held in solution, and their effect when aluminium sulphate is used as a coagulant. Experiments on the precipitation of silicic acid by alkalis in the presence of aluminium salts showed that the optimum hydrogen-ion concentration for the precipitation of the aluminium hydroxide and the removal of the silicic acid is  $1 \times 10^{-8}$ . The limiting values of the hydrogen-ion concentration between which the solid aluminium hydroxide phase is present are  $1 \times 10^{-4}$  and  $1 \times 10^{-11}$ . If the alkali (sodium hydroxide) is added all at once, the presence of silicic acid prevents the precipitation of aluminium hydroxide, apparently by acting as a protective colloid. The presence of bivalent cations, however, destroys this protective power. The effect of a number of electrolytes on the coagulation of clay suspensions by aluminium sulphate was studied. The electrolytes examined, arranged in their order of efficiency as coagulants, were: aluminium sulphate, calcium and barium hydr-

oxides, calcium chloride, magnesium sulphate, magnesium and calcium hydrogen carbonates. The ratio of efficiency of aluminium to calcium and barium ions is about 5 to 1. Sodium hydroxide, hydrogen carbonate, carbonate, and sulphate have a singular influence on the coagulating effect of aluminium sulphate. With a given amount of sodium hydroxide, for example, and gradual addition of aluminium sulphate to the clay suspension, there is first increased dispersion, then coagulation, followed by renewed dispersion and a second coagulation. The second disperse phase is not as stable as the first. The presence of silicic acid has in all cases a retarding effect on the coagulation by aluminium sulphate, whatever salts may be present. E. H. R.

**Emulsions. III.** T. R. BRIGGS [with J. C. ASHMEAD, C. F. TEARS, and L. H. CLARK] (*J. Physical Chem.*, 1920, **24**, 120—126. Compare A., 1915, ii, 531).—The time required to emulsify a series of mixtures of benzene and 1% solutions of sodium oleate has been determined for various methods of mixing. Mechanical shaking, intermittent hand shaking, with measured interval between the shakes, continuous hand shaking, and rolling the bottles containing the mixtures were compared. It is shown that intermittent shaking is far more efficient than uninterrupted shaking, even in a shaking machine. The time and number of shakes required to complete an emulsification both vary with the rest interval between the shakes. Emulsions are easily made by rolling or rotating cylindrical bottles containing oil and soap solution. This method of procedure is similar to the "Continental" method (see following abstract). The ideal emulsifying process is one causing the benzene to break up into drops with the least disintegration of the aqueous soap solution. J. F. S.

**Emulsions. IV.** T. R. BRIGGS, F. R. DU CASSÉ and L. R. CLARK (*J. Physical Chem.*, 1920, **24**, 147—160).—The preparation of emulsions by the continental method is investigated in the case of olive oil. The method consists in preparing an emulsion nucleus by grinding together in a mortar definite quantities of oil, water, and gum, and then diluting with the requisite quantity of water. It is shown that the hypothesis of Roon and Oesper (A., 1917, ii, 299) that hydration of an emulsifying colloid must take place at the moment of disintegrating the oil is not in accordance with experiment. Even in a mortar, emulsions may be made with previously hydrated colloids. Emulsions are easily produced by the method of trituration in a mortar if the area of the interface between oil and water is made sufficiently large. One method by which this may be achieved is to suspend finely divided solids, which are easily wetted, in the oil. The effectiveness of the solid is increased by decreasing the average size of the particles. Up to a certain limit, the readiness with which an emulsion forms increases as the quantity of solid added. It is preferable to suspend the solid in the liquid before adding the

dispersing solution. The most effective solids are those readily wetted by the dispersion medium. In the continental method, gum arabic (acacia) plays the part of finely divided solid and emulsifying colloid. The finely divided solid serves to increase the interface between oil and water. Wetting phenomena may also cause the displacement of one liquid by the other, and consequently give rise to disintegration of the displaced liquid. Emulsions of water in oil may be made in a mortar in the presence of finely divided solids easily wetted by oil. J. F. S.

**Physical Chemistry of Rusting. II. Equilibria in the System Lead-Sulphur-Oxygen.** W. REINDERS (*Zeitsch. anorg. Chem.*, 1919, **109**, 52—62. Compare A., 1915, ii, 47, 773).—A criticism of a paper by Schenck and Albers (A., 1919, ii, 222) on the equilibria in the system lead-sulphur-oxygen, in which it is shown that the experimental results are not trustworthy and will not bear the interpretation put on them. Of the five quintuple points characterised, two are shown to be impossible, and five other equilibrium curves are also not in keeping with known facts. J. F. S.

**Chemical Affinity. XI. The Transformation of Reciprocal Pairs of Salts and the Equilibrium of Benzidine and Benzidine Sulphate.** J. N. BRÖNSTED and AGNES PETERSEN (*K. Danske. Vidensk. Medd. Math. Phys.*, 1917, **1**, No. 3, 1—21; from *Chem. Zentr.*, 1920, i, 425—426. Compare A., 1915, ii, 221).—The affinity of the reaction  $\text{KCl} + \text{NaBr} \rightarrow \text{KBr} + \text{NaCl}$  has been estimated to be 1620 cal. by an electrochemical method, using hydrogen, tartaric acid, and alkali tartrates; the following elements were measured: (1)  $\text{H}_2 | \text{H}_2\text{C}_4\text{H}_4\text{O}_6, \text{KHC}_4\text{H}_4\text{O}_6, \text{KCl} | \text{HgCl}, \text{Hg}$ ; (2)  $\text{H} | \text{H}_2\text{C}_4\text{H}_4\text{O}_6, \text{NaHC}_4\text{H}_4\text{O}_6, \text{H}_2\text{O}, \text{NaCl} | \text{HgCl}, \text{Hg}$ ; (3)  $\text{H} | \text{H}_2\text{C}_4\text{H}_4\text{O}_6, \text{KHC}_4\text{H}_4\text{O}_6, \text{KBr} | \text{HgBr}, \text{Hg}$ ; (4)  $\text{H} | \text{H}_2\text{C}_4\text{H}_4\text{O}_6, \text{NaHC}_4\text{H}_4\text{O}_6, \text{H}_2\text{O}, \text{NaBr}, 2\text{H}_2\text{O} | \text{HgBr}, \text{Hg}$ .

The affinity of the transformation  $\text{KCl} + \frac{1}{2}\text{Na}_2\text{SO}_4 \rightarrow \frac{1}{2}\text{K}_2\text{SO}_4 + \text{NaCl}$  was measured in the following manner. As a consequence of the formation of glaserite, the system of the three salts is unstable, but the two systems  $\text{KCl} + \text{K}_2\text{SO}_4$  and  $\text{NaCl} + \text{Na}_2\text{SO}_4$  are separately completely stable. If sulphuric acid of the same potential is added to each system, the following actions occur:  $\frac{1}{2}\text{H}_2\text{SO}_4 + \text{KCl} = \frac{1}{2}\text{K}_2\text{SO}_4 + \text{HCl}$  and  $\frac{1}{2}\text{H}_2\text{SO}_4 + \text{NaCl} = \frac{1}{2}\text{Na}_2\text{SO}_4 + \text{HCl}$ ; hydrochloric acid is thus liberated at two potentials, the difference of which is a measure of the affinity of the change. The two potentials were measured by hydrogen and calomel electrodes. The authors endeavoured to secure equality in the sulphuric acid potential in the two systems by the addition of a mixture of benzidine and benzidine sulphate, or of the latter alone; it was expected that elimination of sulphuric acid would occur in accordance with the scheme  $\text{C}_{12}\text{H}_8(\text{NH}_2)_2, \text{H}_2\text{SO}_4 \rightarrow \text{C}_{12}\text{H}_8(\text{NH}_2)_2 + \text{H}_2\text{SO}_4$  until the solution had attained a sulphuric acid potential independent of the other components. It was, however, found

that the decomposition of benzidine sulphate by water or aqueous solutions does not take place in such a simple manner, since the addition of benzidine to a solution which was in equilibrium with benzidine sulphate caused a marked decrease of the sulphuric acid potential. Further investigation disclosed the existence of the compounds  $[C_{12}H_8(NH_2)_2]_3 \cdot 2H_2SO_4$  and  $[C_{12}H_8(NH_2)_2]_2 \cdot H_2SO_4$  in addition to the well-known sulphate. By the aid of elements, in which the sulphuric acid potential was maintained constant in the manner indicated, the affinity of the reaction  $KCl + \frac{1}{2}Na_2SO_4$  was estimated to be 210 cal. H. W.

**The Term "Inversion."** J. B. FERGUSON (*Science*, 1919, [N.S.], 50, 544—546).—The following terminology in inorganic chemistry is suggested. Changes such as the passage of rhombic to monoclinic sulphur, the equilibrium temperatures of which are fixed at fixed pressures, regardless of the complexity of the system, provided no solid solutions are formed, are examples of "inversion." Such reactions as the melting of sodium sulphate decahydrate, which occur, under a definite pressure, within a range of temperatures in presence of a third component, are cases of "transition." "Dissociation" is the name given to univariant changes when the compositions of all the phases can be represented by chemical formulæ. J. R. P.

**Proportions of Chlorine and of Hydrogen which Limit the Explosion of Mixtures of these Gases.** PAUL MATHIEU (*J. Physique*, 1917, 7, 166—172).—If a mixture of hydrogen and chlorine is exposed to the radiation from the spark of an induction coil, explosion occurs only when the composition of the mixture is between the limits 91.9% of chlorine and 8.1% of hydrogen and 14.3% of chlorine and 85.7% of hydrogen. When exposed to the radiation of a magnesium flame, the explosive mixtures lie between the limits 90.2% of chlorine and 9.8% of hydrogen and 47.5% of chlorine and 52.5% of hydrogen. The different explosion limits are possibly due to the good conductivity of hydrogen for heat. CHEMICAL ABSTRACTS.

**Hydrolysis of Esters of Polyhydric Alcohols. II.** EIICHI YAMAZAKI (*J. Tokyo Chem. Soc.*, 1919, 40, 667—680).—In this paper are given the experimental data obtained in connexion with the equation previously deduced for the hydrolysis of triacetin to glycerol (this vol., ii, 170). CHEMICAL ABSTRACTS.

**Catalysis. VII. Catalysis in Heterogeneous Systems.** NIL RATAN DHAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, 22, 570—575).—The velocity of solution of anhydrous ferric sulphate in water can be increased by the presence of reducing agents, such as stannous chloride or ferrous sulphate, but no satisfactory explanation of this phenomenon is forthcoming.

When 20% nitric acid in excess acts on copper at 18°, so that



the whole of the copper is dissolved, the action is accelerated by both ferrous and ferric salts, as well as by a number of other salts and compounds. The view hitherto held regarding the part played by ferrous salts in destroying nitrous acid needs to be modified, since it has been shown that nitrous acid is formed by the action of nitric acid on ferrous salts. Oxidising agents like hydrogen peroxide, potassium permanganate, chromic acid, etc., which destroy nitrous acid, retard the action of nitric acid on copper. Finally, there is a small group of substances which in very small concentrations exert a slight accelerating effect, whilst in large concentrations they have a retarding effect (compare T., 1917, 111, 707). W. G.

**The Effect of Surface Oxidation on some Metallic Catalysts.** FRANK F. RUPERT (*J. Amer. Chem. Soc.*, 1920, 42, 402—411).—The observation reported by Wigand (*Sitzungsber. Ges. Naturwiss. Marburg*, 1907, p. 33) that platinum foil which has been used as an electrode acquires an increased catalytic activity towards detonating gas (electrolytic hydrogen-oxygen mixture) has been confirmed by the author. The increased activity, however, is confined to the anode; it is due to surface oxidation, and can be induced by chemical means as well as by anodic polarisation. The surface oxidation probably consists in the formation of a film of surface-combined oxygen of atomic dimensions. Increase of catalytic activity by anodic polarisation was also found in the case of palladium and of gold; in the case of cobalt, a slight increase detected was probably due to increase of the active surface by etching. An estimation of the comparative order of magnitudes of the activities of the metals examined gives 50:1 for the ratio of palladium to platinum, 2000:1 for platinum to gold, and 200:1 for platinum to cobalt. The results obtained contradict Sackur's conclusions with regard to the effect of polarisation on the catalytic activity of metals (A., 1906, ii, 261). E. H. R.

**Do Simple Numerical Relationships Exist between the Linear Dimensions of the Atoms?** MARIANO PIERUCCI (*Nuovo Cim.*, 1920, [vi], 19, i, 109—115).—The author assumes that only at the absolute zero of temperature is it possible for the atomic volume to represent the true volume of the atoms. On this assumption, he calculates the cube root of the atomic volume at absolute zero for those elements which (1) have a known density in the solid state, and (2) have a coefficient of thermal expansion which either is known at low temperatures or is known and very small at ordinary temperatures. To this cube root he gives the name *atomic radius*. The necessary data are taken from Landolt's tables, and are known, in some instances only approximately, for twenty-nine elements. The results obtained appear to suggest that the atomic radii of all elements are integral multiples of one and the same length. T. H. P.

**Electron Ring Model and the Electrical Moment of some Dipolar Molecules.** LÉON SCHAMES (*Physikal. Zeitsch.*, 1920, 21, 156—158. Compare this vol., ii, 172).—The electrical moment ( $M$ ) of diatomic molecules is considered theoretically, and equations are developed by which this factor, and other factors connected with the structure of molecules, may be calculated. Calculations are carried out for the molecules of carbon monoxide, hydrogen chloride, water, and carbon dioxide, and the following values obtained;  $h$  is the distance between the two nuclei of effective charge number  $n_1$  and  $n_2$ , respectively, and mass  $m_1$  and  $m_2$ ;  $r_1$  and  $r_2$  are the distances of the nuclei from the mechanical centre of gravity, and  $d_1$  and  $d_2$  their distances from the electron ring;  $a$  is the radius of the ring of  $n$  electrons,  $\omega$  is the angular velocity of the electrons in the ring, which is calculated from the quanten equation  $na^2\omega = kh/2\pi$ , where the quanten number  $k$  for the second and third ring is equal to 2;  $x$  is the fraction of  $h$  where the electrical centre of gravity of the ring lies, and  $yh$  is the distance the electrical centre of gravity of the nucleus lies from the nucleus  $n$ , that is,  $y = n_2/n$ ;  $l$  is the length of the dipole, and the other symbols have their usual meaning. Carbon monoxide,  $P = 10.07 \times 10^{-40}$ ,  $Q = 10.07 \times 10^{-40}$ ,  $n_1 = 6$ ,  $n_2 = 4$ ,  $h = 0.951 \times 10^{-8}$ ,  $r_1 = 0.4075 \times 10^{-8}$ ,  $r_2 = 0.5435 \times 10^{-8}$ ,  $x = 0.184$ ,  $y = 0.400$ ,  $d_1 = 0.175 \times 10^{-8}$ ,  $d_2 = 0.776 \times 10^{-8}$ ,  $a = 0.713 \times 10^{-8}$ ,  $\omega = 4.60 \times 10^{16}$ ,  $l = 0.205 \times 10^{-8}$ , and  $M = 9.70 \times 10^{-18}$ . Hydrogen chloride,  $P - Q = 2.7 \times 10^{-40}$ ,  $n_1 = 7$ ,  $n_2 = 1$ ,  $h = 1.31 \times 10^{-8}$ ,  $r_1 = 0.036 \times 10^{-8}$ ,  $r_2 = 1.274 \times 10^{-8}$ ,  $x = 0.0034$ ,  $y = 0.125$ ,  $d_1 = 0.0045 \times 10^{-8}$ ,  $d_2 = 1.3055 \times 10^{-8}$ ,  $a = 0.786 \times 10^{-8}$ ,  $\omega = 3.78 \times 10^{16}$ ,  $l = 0.159 \times 10^{-8}$ ,  $M = 6.02 \times 10^{-18}$ . Water,  $P = 2.21 \times 10^{-40}$ ,  $Q = 1.25 \times 10^{-40}$ ,  $R = 0.96 \times 10^{-40}$ ,  $n_1 = 6$ ,  $n_2 = 1$ ,  $h = 0.657 \times 10^{-8}$ ,  $b = 0.542 \times 10^{-8}$ ,  $r_1 = 0.0734 \times 10^{-8}$ ,  $r_2 = 0.796 \times 10^{-8}$ ,  $x = 0.027$ ,  $y = 0.250$ ,  $d_1 = 0.0177 \times 10^{-8}$ ,  $d_2 = 0.639 \times 10^{-8}$ ,  $a = 0.402 \times 10^{-8}$ ,  $\omega = 14.4 \times 10^{16}$ ,  $l = 0.146 \times 10^{-8}$ ,  $M = 1.87 \times 10^{-18}$ . Carbon dioxide,  $P = 9.40 \times 10^{-40}$ ,  $Q = 5.83 \times 10^{-40}$ ,  $R = 3.57 \times 10^{-40}$ ,  $n_1 = 4$ ,  $n_2 = 6$ ,  $h = 0.708 \times 10^{-8}$ ,  $b = 0.262 \times 10^{-8}$ ,  $r_1 = 0.515 \times 10^{-8}$ ,  $r_2 = 0.325 \times 10^{-8}$ ,  $x = 0.90$ ,  $y = 0.75$ ,  $d_1 = 0.637 \times 10^{-8}$ ,  $d_2 = 0.071 \times 10^{-8}$ ,  $a = 0.485 \times 10^{-8}$ ,  $\omega = 9.92 \times 10^{16}$ ,  $l = 0.106 \times 10^{-8}$ ,  $M = 8.01 \times 10^{-18}$ . J. F. S.

**Twenty-sixth Annual Report of Committee on Atomic Weights. Determinations Published during 1918 and 1919.** GREGORY PAUL BAXTER (*J. Amer. Chem. Soc.*, 1920, 42, 327—333).—Papers published during 1918 and 1919 dealing with atomic weight determinations are summarised. E. H. R.

**Arrangement of Electrons in the Elements of the Long Periods.** RUDOLF LADENBURG (*Naturwiss.*, 1920, 8, 5—11; from *Chem. Zentr.*, 1920, i, 315—316).—The arrangement of electrons postulated by Kossel (A., 1919, ii, 408) gives satisfactory results as far as scandium. For elements of higher atomic weight, how-

ever, it must be replaced by another conception, since it demands a definite prevalent valency, whilst the elements from titanium to zinc and from zirconium to cadmium exhibit a series of mobile valency stages, and, also, the maximal valency, so far as such can be spoken of, does not increase from member to member, but remains constant. Peculiar physical properties, such as magnetism of the elements and colour of the elementary ions, are associated with the change in chemical behaviour. Both properties are dependent on conditions under which the readily separable outermost valency electrons are already detached. Those elements which are paramagnetic and have small atomic volumes yield coloured, positively charged ions in the dissolved state and in glasses and precious stones. To account for the peculiar position of the elements of the series mentioned above, the author considers that the outermost zone of all the elements from titanium to zinc, and from yttrium to cadmium (except copper and silver), contains two electrons. The common metallic character of the majority of these elements, and the fact that they are at least positively bivalent in their heteropolar compounds, thereby find their expression. The sharp maxima of the atomic volumes of the alkali metals indicate that with them a new electron zone commences; this is certainly not the case with copper, silver, and gold, the atomic volumes of which lie near the minima, and are scarcely to be distinguished from the neighbouring elements. The new electrons of the elements titanium, vanadium, chromium, etc., must migrate into the interior of the outermost zone, but are supposed to form an intermediate zone between the two outer ones previously described, since they can participate in chemical reactions in the same manner as the electrons of the outermost zone, but have greater freedom of motion than these, and can also be separated singly; an explanation of the varying valency of these elements is thus given. In the cases of zinc and cadmium, in which the number of electrons in the intermediate zone is already increased to ten, a stable arrangement similar to that of the noble gases is postulated, so that an electron of this zone cannot be detached in exchange with other atoms. In the cases of gallium and indium, the new electrons take their place in the outer zones (as in the short periods), which in the corresponding rare gases (krypton and xenon) contain eight electrons. The assumption of the intermediate zones facilitates the understanding of the relationship between the colour of the ions and the periodic system. It is thereby assumed that the electrons of the intermediate zone, when the latter is incomplete and contains less than ten electrons, are more readily displaced by the energy of visible light, and, in accordance with Bohr's conception of emission and absorption, absorb the corresponding energy and pass to a path of greater energy. Absorption in the ultra-violet must be accomplished by electrons of other, more complete zones. Although an analogy must exist between the colour of the ions and the variable valency, since each property is ascribed to the looseness of the attachment

of the electrons in the incomplete intermediate zone, a complete agreement between these properties is not to be expected. The connexion between colour and ability to form compounds depends on the amounts of energy which are required for the absorption of light on the one hand, and for the production of another degree of combination on the other. The quantities of energy are related in the same manner as the resonance potential and ionisation tension in the line spectra of metals. Doubtless, coloured compounds can exist in which the intermediate zone is absent, but mobility of the electrons is due to other influences. The simultaneous appearance of colour in the ions and of paramagnetism in the periodic scheme indicates that the latter is also caused by the electrons of the intermediate zone, although it is acknowledged that the latter phenomenon is but little understood. The distinctive characteristics of the electrons of the magnetic elements are still less obvious, and are not expressed in the author's scheme. The latter is, however, only to be regarded as a preliminary conception.

H. W.

**New Periodic Relationship between the Atomic Weights of the Chemical Elements.** KARL FEHRLE (*Physikal. Zeitsch.*, 1920, **21**, 162—166. Compare A., 1918, ii, 296).—A theoretical paper in which, on the basis of the quantum theory, an expression is evolved whereby the atomic weight of the elements may be calculated. The calculation is based on the atomic model previously described by the author (*loc. cit.*). The atomic weight is calculated by means of the formula  $A = \sum_1^n \sqrt{67 \cdot 7 + (n-1)16 \cdot 59}$ , where  $n$  is the number of sheaths in the atom. The calculated atomic weights run parallel with the experimental values, and the difference between the two is a periodic function of the atomic weight. The cause of this periodic function is to be found in the characteristic vibrations of the molecule in relationship to those of its atoms.

J. F. S.

**Inter-relationship of the Chemical Elements.** HAWKSWORTH COLLINS (*Chem. News*, 1920, **120**, 169—170).—The author has picked out nine pairs of elements, the sum of the atomic weights of each pair of which approximate to that of vanadium; six pairs, the sum of the atomic weights of which approximate to that of chromium; and eight pairs, the sum of the atomic weights of which approximate to that of manganese. In these tables, three sets of coincidences are apparent: (i) The sum of the valencies of each pair is equal to the valency of the element under consideration in seventeen cases out of twenty-three. (ii) The sum of the valencies of each pair is odd or even according as the valency of the element under consideration is odd or even. (iii) The sum of each pair of atomic weights is greater than the integer which is nearest to the atomic weight of the element under consideration in twenty cases out of twenty-three, when the atomic weight of oxygen is taken as sixteen, and is less than the same in nineteen cases out

of twenty-three when hydrogen is taken as the unit. It is shown that the probability that the first coincidence is due to chance is one to several billions, that the second is a chance or accident is one to eight millions, and that the third is a chance or accident is one to four thousand millions. The author concludes, therefore, that these relationships are due to some general similarity in the formation of the elements. [See also A., 1919, ii, 106.]

J. F. S.

**Dependence of the Valency Number on Temperature. III. The Systematic Doctrine of Affinity. X.**

WILHELM BILTZ (*Zeitsch. anorg. Chem.*, 1919, **109**, 132—144. Compare A., 1915, ii, 440, 465, 466).—A theoretical paper in which the dependence of the valency exercised by various elements at different temperatures is considered. The dissociation of the higher chlorides of gold, platinum, iridium, and vanadium, the oxides of iron, uranium, and lead, the crystalline hydrates of uranyl nitrate and certain sulphides is discussed, and the dissociation represented as valency isobars. From this consideration, it is shown that the valency isobars are steeper the lower the temperature of the starting point. This rule, however, is not absolute, for when substances which have dissimilar constitutions are considered, it fails entirely. The constitutive influences are considered in connexion with the metal amines. The temperature range over which the amines of the chlorides of the metals manganese, iron, cobalt, and nickel are stable is tabulated. In the case of the hexamines, that of nickel iodide has the greatest temperature range of existence ( $177.5^{\circ}$ ), and that of manganese chloride the least. The order of existence increases from manganese to iron, cobalt, and nickel, and from chloride to bromide and iodide. In the case of the diamines, the range of existence increases from chloride to bromide, and falls again to the iodide to a value lower than that for the chloride; it also increases from manganese to iron, and then falls to cobalt and nickel. It is found in the monamines that the existence range falls from chloride to iodide and from manganese to nickel.

J. F. S.

**Calculation of the Chemical Constants of Polyatomic Gases from the Planck Theory of Probabilities.**

LÉON SCHAMES (*Physikal. Zeitsch.*, 1920, **21**, 158—159. Compare this vol., ii, 172).—It is shown that the strict calculation from the Planck probability theory leads to the same result as the Sackur-Tetrode calculation (*loc. cit.*). It is shown that  $\sqrt[3]{PQR} = 0.94 \times 10^{-40}$  for water according to the Sackur-Tetrode calculation, but from the rotation spectrum, according to Planck's first theory, the value is  $1.38 \times 10^{-40}$ , and from the Planck second theory  $2.48 \times 10^{-40}$ . No reason can, as yet, be given for the discrepancy.

J. F. S.

**Graphic Mixture Calculations.** WA. OSTWALD (*Chem. Zeit.*, 1920, **44**, 241—242).—When it is required, from two or more

materials containing two or more constituents in known proportions, to produce another mixture containing the same constituents in other proportions, the calculation can be greatly simplified by the use of the graphic method. In more complicated cases, an exact solution of the problem may be impossible, and the graphic method then affords a ready means of obtaining an approximate solution.

E. H. R.

### Measurements of the Volume of the Mercury Meniscus.

J. PALACIOS (*Anal. Fis. Quim.*, 1919, **7**, 275—295).—Exact determinations have been made of the volume occupied by the meniscus of mercury in glass tubes 5, 6, 7, 8, 9, 10, and 11 mm. in diameter, and with heights of meniscus varying by 0.1 mm. from 0.1 mm. to 2.1 mm. The author draws attention to a constant appreciable difference between his results and those of Scheel and Heuse (*Ann. Physique*, 1910, **33**, 291), and suggests that an error of 0.04 mm. for the radius of the tube used by Scheel and Heuse would account for the discrepancies.

W. R. S.

### Apparatus for the Extraction of Liquids.

KURT BRAUER and ERWIN W. EBERT (*Chem. Zeit.*, 1920, **44**, 214).—An apparatus of the Soxhlet type is described for the extraction of a liquid with a solvent of greater density. In place of the usual siphon of the apparatus, a tube is provided extending upwards from the bottom of the main cylinder and entering the side (vapour) tube at about two-thirds the height of the latter. As the heavy solvent collects below the liquid undergoing extraction, it flows gradually back through the side-tube into the extraction flask. A tap is provided between the cylinder and stem of the apparatus.

W. P. S.

### Lecture Experiment on Combustion.

A. PRICE (*Chem. News*, 1920, **120**, 149—150).—A Bunsen burner is made with a long, wide glass tube in place of the usual metal tube, and a little above the top of the tube a wire is clamped at right angles to it. The gas is turned on so that a mixture of coal-gas and air ascends the tube, as in the ordinary Bunsen burner. By carefully lowering a small flame on to the wire, with possibly a little adjustment of the gas supply, the gas can be made to burn indefinitely from the top of the wire with a very pale blue, luminous flame. The flame can similarly be made to burn from a small, rounded object, such as a bullet, suspended above the tube by a fine wire. The continuance of the phenomenon depends on the mixed gases coming up the tube at a certain velocity, too great for combustion to take place at the end of the tube. The presence of the wire or small object lowers the velocity sufficiently to permit the gases to burn. When the velocity is lowered sufficiently by cutting off the gas supply, the flame strikes back to the jet at the bottom of the tube.

E. H. R.

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### Inorganic Chemistry.

**The Purification of Liquefied and Compressed Gases for Laboratory Purposes.** L. MOSER [and, in part, W. FOLTZ] (*Zeitsch. anorg. Chem.*, 1920, **110**, 125—142).—An account is given of the impurities likely to be present in those gases which are supplied commercially in cylinders, and of the best means for purifying the gases. Carbon dioxide, which is obtained commercially by heating a metal hydrogen carbonate solution, contains 1—2% of impurity. It can be completely freed from oxygen by passing it at a rate of 4 to 6 litres per hour through a paste of chromium acetate, and then through a 15% solution of titanous chloride acidified with hydrochloric acid, or by passing over red-hot copper at 4 to 10 litres per hour. Carbon monoxide can be removed by passing the gas over asbestos carrying finely divided cuprous oxide at 700—800°, hydrogen sulphide by copper sulphate on pumice stone, and sulphur dioxide by a solution of potassium permanganate. Commercial nitrogen, prepared by the Linde process, has only to be freed from traces of oxygen. The best wet absorbent is copper gauze in ammonium carbonate solution, the gas being subsequently passed through concentrated sulphuric acid to absorb ammonia. It can finally be passed over copper asbestos at 700—800° to remove the last trace of oxygen. Electrolytic hydrogen is practically pure, but that prepared from water gas by the Linde process may contain air, oxides of carbon, and sometimes arsine. Further, through the action of the carbon monoxide on the steel cylinder under pressure, iron pentacarbonyl is formed, and the hydrogen may contain more than 3% of it. Owing to the difficulty of removing this impurity or the carbon monoxide formed by its decomposition, such hydrogen is unsuitable for laboratory use. Commercial oxygen, prepared by the Linde process, contains only traces of nitrogen, which cannot be removed by chemical means, and a trace of carbon dioxide, which can be removed by soda-lime. Electrolytic oxygen may contain as much as 4% of hydrogen, which can be burnt to water by passing the gas over heated platinised asbestos. Commercial chlorine, generally of electrolytic origin, can be freed from air and oxides of carbon by liquefying in a tube immersed in a mixture of ether and carbon dioxide and redistilling, and commercial sulphur dioxide can be purified in the same way, although it is pure enough for most purposes. Commercial ammonia contains about 2% of impurity, consisting of water and organic substances, such as pyridine, methylamine, and pyrrole. The gas can be dried by means of lime or soda-lime, but the organic impurities are difficult to remove. E. H. R.

**Determination of the Boiling Point of Sulphur by means of the Nitrogen Thermometer.** P. CHAPPUIS (*Bur. Int. Poids. Mes.*, 1917, *Mem.* **16**, 44 pp.).—The b. p. of sulphur at normal

pressure, determined by measuring the increase of pressure at constant volume of nitrogen (prepared from a solution of sodium nitrite, ammonium sulphate, and potassium chromate, and washed with a mixture of potassium dichromate and sulphuric acid and then with potassium hydroxide) in a silica bulb of capacity approximately 247 c.c., was found to be  $444.60^\circ$  on the thermodynamic scale.

The original paper should be consulted for details of the apparatus employed and the corrections made.

## CHEMICAL ABSTRACTS.

**Action of Hydroxylamine on Sodium Tetrathionate.**

A. GUTMANN (*Ber.*, 1920, **53**, [B], 444—446).—In acid solution, hydroxylamine oxidises the sulphite residue in tetrathionic acid to sulphuric acid, and is itself reduced to ammonia,  $\text{H}_2\text{S}_4\text{O}_6 + \text{NH}_2\cdot\text{OH} + \text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 + 2\text{S} + \text{NH}_3$ . In alkaline solution, on the other hand, the loosely combined oxygen atom of the tetrathionate oxidises hydroxylamine to nitrous or nitric acid,  $\text{Na}_2\text{S}_4\text{O}_6 + 2\text{NH}_2\cdot\text{OH} + 3\text{NaOH} = 2\text{Na}_2\text{S}_2\text{O}_3 + \text{NaNO}_2 + 3\text{H}_2\text{O} + \text{NH}_3$ .

H. W.

**The Decomposition Equilibrium of Nitrosyl Bromide and the Proof of (the Formation of) the Tribromide,  $\text{NOBr}_3$ .**

MAX TRAUTZ and VASANJI P. DALAL (*Zeitsch. anorg. Chem.*, 1920, **110**, 1—47).—A continuation of previous work (A., 1918, ii, 162). The equilibrium between nitric oxide, bromine, and their reaction products was studied between  $-15^\circ$  and  $330^\circ$  by the method previously described (compare Trautz and Wachenheim, A., 1917, ii, 74), with bromine pressures between 13 and 500 mm., and nitric oxide pressures between 28 and 900 mm. Equilibrium is attained very rapidly, and the reaction is the most rapid which has yet been studied. For low bromine pressures, below 50 mm., and at temperatures above  $140^\circ$ , the amount of the tribromide formed appears to be negligible, and the reaction  $2\text{NO} + \text{Br}_2 \rightleftharpoons 2\text{NOBr}$  can be regarded as of the third order. As is to be expected from the small heat of reaction, the reaction is more rapid than the formation of nitrosyl chloride. The velocity constant is, at  $-15^\circ$ ,  $k = 1.1 \times 10^{-10}$ .

An independent proof of the existence of nitrosyl bromide and nitrosyl tribromide was obtained from an investigation of the fusion-point diagram of the reaction products of bromine and nitric oxide. The fusion curve shows a eutectic of bromine and nitrosyl tribromide, a maximum at  $-40^\circ$  corresponding with  $\text{NOBr}_3$ , a second eutectic of  $\text{NOBr}_3$  and  $\text{NOBr}$  in the neighbourhood of  $-60^\circ$ , and a second maximum corresponding with  $\text{NOBr}$  at about  $-55^\circ$ . Nitrosyl tribromide was found to be a brownish-black, almost opaque liquid which begins to boil, with partial decomposition, at about  $32^\circ$ . It has  $D_4^{20} = 2.637$ , which agrees closely with Landolt's value, 2.628 at  $22.6^\circ$ . The fusion diagram does not confirm or exclude the existence of nitrosyl dibromide



among the products. The heats of formation of the mono- and tri-bromide were calculated from measurements made of their heats of reaction in aqueous solution with potassium hydroxide. The significance of the results obtained cannot be exactly estimated, because the extent of decomposition of liquid NOBr and NOBr<sub>3</sub> is unknown, but probably the heat of formation of NOBr is between 9000 and 10,500 cal., and of NOBr<sub>3</sub> between 22,000 and 27,000 cal., at 22°. The results obtained for the equilibrium constants and for the heats of formation agree, in general, with theory. It is concluded that, in liquid mixtures of the components at low temperatures, the principal product is nitrosyl tribromide, in gaseous mixtures rich in bromine at moderate temperatures, nitrosyl dibromide, and under other conditions, nitrosyl bromide or its decomposition products.

E. H. R.

**War Experiences in the Manufacture of Nitric Acid and the Recovery of Nitrous Fumes.** JAMES WALKER (T., 1920, 117, 382—389).—A lecture delivered before the Chemical Society on December 18th, 1919.

**Interaction of Phosphorus Haloids and Arsenious and Arsenic Compounds.** NAGENDRA NATH SEN (*J. Proc. Asiatic Soc. Bengal*, 1919, 15, 263—265).—When a few drops of phosphorus trichloride are added to an aqueous solution of arsenious oxide, the solution turns yellow, then opaque-brown, and finally a copious precipitate of arsenic is thrown down. The arsenic is amorphous, apparently a new allotropic form, insoluble in carbon disulphide. The reaction does not take place when phosphorous acid is used or when the phosphorus trichloride is first dissolved in water. With phosphorus tribromide and tri-iodide, the same reaction takes place, but more slowly, and in the latter case the precipitate is contaminated with red phosphorus. Unlike the trichloride, the tribromide and tri-iodide still bring about the reaction if they are first dissolved in water. It appears, therefore, that an intermediate compound is first formed when the phosphorus haloid dissolves in water, but that, in the case of the trichloride, this intermediate compound is more rapidly decomposed than in the cases of the other haloids. The reduction, which takes place with both arsenites and arsenates, is brought about by the intermediate compound. The reaction is very delicate, and with phosphorus trichloride the presence of 0.000075 gram of arsenic per c.c. can be detected. Antimonious and antimonious compounds do not give the reaction. The course of the reduction is probably given by the equation  $As_2O_3 + 3PCl_3 + 9H_2O = 2As + 3H_2PO_4 + 9HCl$ .

E. H. R.

**Coagulation of Metal Sulphide Hydrosols. II. Influence of Temperature on the Rate of Coagulation of Arsenious Sulphide Hydrosols.** JĀNENDRA NATH MUKHERJEE (T., 1920, 117, 350—358).

**Charcoal before the War. I.** WILDER D. BANCROFT (*J. Physical Chem.*, 1920, **24**, 127—146).—A theoretical paper in which the composition and structure of various forms of charcoal are discussed. J. F. S.

**Some Properties of Charcoals.** H. E. CUDE and G. A. HULETT (*J. Amer. Chem. Soc.*, 1920, **42**, 391—401).—When the density of charcoal is determined by the water immersion method, a gradual increase in weight of the immersed charcoal is observed, the maximum weight only being reached after many days. The same occurs when other liquids, such as carbon disulphide, benzene, or carbon tetrachloride, are used instead of water, and in each case the final density found for the charcoal is different. Quantitative experiments were made with a sample of cocoanut charcoal, 18—20 mesh, and the maximum densities found were: with water, 1.854; with carbon disulphide, 1.984; with benzene, 1.797; and with carbon tetrachloride, 1.647. The change in weight of the immersed charcoal with time is due to the progressive penetration of the liquid into the charcoal, rapidly at first, then more slowly. The rate of penetration and the final density found appear to vary in proportion to the surface tension and inversely with the viscosity of the liquid. The smaller the size of grain of the charcoal, the greater is the density found, and with the smallest grains obtainable, 0.001 mm. in diameter, using water as the liquid, the final density 1.900 was obtained. High pressure causes rapid penetration, and the 18—20-mesh charcoal in water under 8600 atm. gave a density of 1.902 in the course of a comparatively short time. E. H. R.

**Activation of Wood-charcoal by Heat Treatment.** JAMES C. PHILIP, SYDNEY DUNNILL, and OLIVE WORKMAN (T., 1920, **117**, 362—369).

**Oxidation of Carbon Monoxide.** KARL HOFMANN (D.R.-P. 307614; from *Chem. Zentr.*, 1920, ii, 446).—The process is effected by chromic acid solution to which mercuric oxide has been added. The presence of the latter substance so accelerates the oxidation of carbon monoxide that this gas can be removed from its mixtures with air and other gases with sufficient rapidity for analytical and hygienic purposes. H. W.

**Carbonyl Chloride.** E. PATERNO and A. MAZZUCHELLI (*Gazzetta*, 1920, **50**, i, 30—53).—The carbonyl chloride was prepared by the action of fuming sulphuric acid on carbon tetrachloride, and was purified by distillation with the help of a dephlegmator maintained at constant temperature. A special apparatus was designed for storing the chloride obtained and for delivering small amounts of it as required.

The density of liquid carbonyl chloride, measured by means of a dilatometer with a graduated capillary tube at temperatures

between  $-15.4^{\circ}$  and  $+59.9^{\circ}$ , is expressed well by the formula  $D=1.4264-0.002326t$ ,  $t$  being in degrees Centigrade.

Determinations have been made of the orthobaric density of liquid carbonyl chloride and its vapour by means of Ter-Gazarian's modification (A., 1906, ii, 423) of Young's process, the temperatures employed lying between  $60.3^{\circ}$  and  $181.6^{\circ}$ . In accordance with the rectilinear diameter law of Cailletet and Mathias, the sum of the densities of the liquid and vapour varies very nearly linearly with the temperature, the maximum divergences being less than 0.3%. The whole of the results agree well with the expression  $1.4277-0.00214t$ , whilst for temperatures above  $111^{\circ}$ , for which the diameter is more certainly rectilinear, the formula  $1.4380-0.0022t$  holds.

Comparison of the orthobars of carbonyl chloride and *n*-pentane (see Young, T., 1897, 71, 455) gives for the critical temperature of carbonyl chloride the value  $187^{\circ}$ , which should be accurate to within  $1-2^{\circ}$ . The two expressions given above then lead to the respective values 0.5137 and 0.5133 for the critical density. The conclusions arrived at by Young from considerations based on the law of the rectilinear diameter show that for carbonyl chloride this diameter is convex towards the axis of temperature, and also lead to the provisional value 51.5 atmos. for the critical pressure. According to Mathias, the extrapolated density at absolute zero is three times the critical density, but for carbonyl chloride, such extrapolated density, calculated in accordance with Mendeléev's formula, is almost exactly four times the critical density.

Measurements of the surface tension of carbonyl chloride have been made by means of Ramsay and Shields' method (T., 1893, 63, 1094), the values obtained for  $\gamma=ga^2(d-\sigma)/2$  being 19.51 at  $16.7^{\circ}$ , 17.10 at  $34.5^{\circ}$ , and 15.42 at  $46.1^{\circ}$ . The so-called molecular tension,  $G=\gamma(M/S)^{\frac{1}{2}}$ , has the mean value 2.05, which agrees well with the value 2.12 given by Ramsay for non-polymerised compounds.

Various series of measurements of the vapour pressure at temperatures ranging from about  $-23^{\circ}$  to  $+25^{\circ}$  have been made, the results being in satisfactory agreement with the formula  $\log p=7.5995-1326/T$ ,  $p$  being the absolute pressure in mm. of mercury at the latitude of Rome and  $T$  the absolute temperature. This formula indicates the boiling point of carbonyl chloride to be  $8.02^{\circ}/760$  mm., whereas Beckmann (*Zeitsch. anorg. Chem.*, 1907, 55, 371) found  $8.2^{\circ}/756$  mm.

Berthelot's statement that carbonyl chloride dissolves unaltered to the extent of 2—3 vols. in water, and that it reacts with the latter only slowly, has been contested by recent authors (compare Grignard and Urbain, A., 1919, ii, 340). The authors find that the chloride cannot exist for an appreciable time in contact with pure water, but that the products, carbon dioxide and hydrochloric acid, which it forms with the water hinder further action; in the case of gaseous carbonyl chloride, the carbon dioxide forms an inert separating layer at the surface of the liquid, whilst with

liquid carbonyl chloride it is saturation with hydrogen chloride of the water in immediate contact with the liquid to which retardation of the reaction is due. The action is therefore dependent essentially on diffusion.

Retardation of the reaction between carbonyl chloride and water is caused by acids in general. Attempts made to measure the velocity of the reaction in presence of sulphuric acid by measuring the volumes of carbon dioxide evolved in different periods of time led to irregular results, but showed that the reactivity of sulphuric acid solutions with carbonyl chloride diminishes continuously with increase in the concentration of the sulphuric acid and with fall in the temperature. No hypothesis is advanced to explain this effect of acids, which is due, undoubtedly, to a true retardation of the reaction, and not to a displacement of the equilibrium.

The reaction between carbon tetrachloride and fuming sulphuric acid is not limited to that expressed by the equation  $\text{CCl}_4 + 2\text{SO}_3 = \text{S}_2\text{O}_5\text{Cl}_2 + \text{COCl}_2$ , since in presence of excess of the hot fuming acid, the reaction  $\text{CCl}_4 + 4\text{SO}_3 = 2\text{S}_2\text{O}_5\text{Cl}_2 + \text{CO}_2$  takes place.

If kept at a temperature below  $0^\circ$ , liquid carbonyl chloride absorbs gaseous chlorine in large proportions. At  $-15^\circ$  and under the ordinary pressure, a golden-yellow liquid containing 28.3% of free chlorine is formed; the vapour pressures of this liquid at different temperatures exhibit satisfactory agreement with the law stating that, in mixtures of similar and non-polymerised liquids, the partial pressure of any component is equal to the pressure of the pure component multiplied by its molecular percentage in the mixture.

Carbonyl chloride is absorbed in considerable proportions by heavy lubricating oils, from which it is expelled rapidly and almost completely by a current of air.

T. H. P.

**The Production of Helium and Neon in Discharge Tubes containing Hydrogen.** ARNALDO PIUTTI and ETTORE CARDOSO (*Gazzetta*, 1920, **50**, i, 5—23).—The authors have carried out a number of experiments on the action of the discharge between aluminium electrodes on hydrogen prepared by the electrolysis of dilute sulphuric acid and carefully purified. By means of the spectroscope employed, the neon contained in 0.05 c.c. of air could be detected with ease. After the subjection of the hydrogen to the action of the discharge, the gas was burnt in oxygen prepared by heating potassium permanganate and carefully purified before use; the burnt gases were extracted and purified, and the residue examined spectroscopically. The apparatus used is briefly described. The pressure maintained during the discharge, which occupied from one to twelve hours, varied in different experiments between 0.1 mm. and 3 mm., the temperature prevailing being also varied in different cases.

In no single case was the formation of helium or neon in the tubes detectable, this result being in agreement with that of Strutt

(A., 1914, ii, 201) and in contradiction to that of Collie, Patterson, and Masson (A., 1914, ii, 847; compare Baly, Annual Report, 1914, 45).  
T. H. P.

### **The Solubility of Potassium Bromide in Bromine Water.**

ALFRED FRANCIS JOSEPH (T., 1920, 117, 377—381).

**Formation of Mixed Crystals of Potassium and Ammonium Nitrates at the Ordinary Temperature.** CAILLART (*Bull. Soc. franç. Min.*, 1918, 41, 21—30; from *Chem. Zentr.*, 1920, i, 358).—The work is an extension of that of Wallerant (A., 1906, ii, 151), who has investigated the formation of the mixed crystals from the molten salts. The method suffers particularly from the drawback that the crystals remain in a metastable condition outside the limits of their stability. The author has therefore investigated the crystals deposited from aqueous solutions at a constant temperature, 17°. Difficulties are encountered owing to the great disparity in the solubilities of the salts and to the poor development of the mixed crystals rich in ammonium nitrate, which almost prevents measurement. Crystallographic methods are therefore supplemented by optical ones. The solubility curves of mixtures of the two salts, and the graphs showing the relationship between the composition of the mixed crystals and that of the mother liquors, have been studied in particular, and are found to be composed of three segments corresponding with three types of mixed crystals: (1) rhombic crystals of the potassium nitrate type containing 0—17.2 molecules of ammonium nitrate per 100 molecules of mixture, (2) monoclinic crystals with 55—94.5 molecules of ammonium nitrate per 100 molecules of mixture, and (3) rhombic crystals of the ammonium nitrate type with 98—100 molecules of ammonium nitrate per 100 molecules of mixture. Two types of mixed crystals separate at each concentration, corresponding with the two points of intersection of the curves.

H. W.

### **Influence of Various Metals on the Decomposition of Sodium Amalgam by Water.**

ERICH MÜLLER and ALFRED RIEDEL (*Zeitsch. Elektrochem.*, 1920, 26, 104—109).—The rate of decomposition of water by 0.2% sodium amalgam in the presence of metallic and other substances has been determined. The amalgam (80 grams) was rapidly stirred with 50 c.c. of water and a piece of the metal in question, and the hydrogen collected and measured. The experiments were carried out with ferromolybdenum, cast iron, wrought iron, iron carbide, silicon, ferro-silicon, ferro-vanadium, ferro-tungsten, chromium, platinum, palladium, iridium, nickel, cobalt, manganese, tantalum, graphite, and ferric oxide. It is shown that the iron alloys of molybdenum, vanadium, tungsten, and chromium have a very strong catalytic action on the process. This action depends on the increase in the surface of the amalgam due to the solution, and subsequent separation of the metals. The possibility of applying this action to

the manufacture of sodium hydroxide by the mercury electrode process is considered, and it is shown that if the finely divided catalyst can be entirely removed from the mercury at the end of the process, then it will be advantageous to add the catalyst to the electrolyte in the mercury cells, but if it is not possible to entirely remove the catalyst, then the total current will not be used in the formation of amalgam, but a portion will be used in the liberation of hydrogen.

J. F. S.

**Behaviour of Magnesium Nitride towards Carbon Monoxide and Carbon Dioxide.** FR. FICHTER and CHRISTOPH SCHÖLLY (*Helv. Chim. Acta*, 1920, **3**, 298—304).—The statement of Briegleb and Geuther (1862) that magnesium nitride reacts with carbon monoxide and carbon dioxide to give magnesium oxide, cyanogen, and carbon, and, in the latter case, nitrogen also, is erroneous. Quantitative experiments show that the decomposition of the freshly prepared nitride at 1250° in a stream of the respective gases is expressed by the following equations:  $\text{Mg}_3\text{N}_2 + 3\text{CO}_2 = 3\text{MgO} + 3\text{CO} + \text{N}_2$  and  $\text{Mg}_3\text{N}_2 + 3\text{CO} = 3\text{MgO} + \text{N}_2 + 3\text{C}$ . Carbon monoxide causes no change at 750°, and reacts less readily than carbon dioxide. The reactions are considered to follow on the dissociation of the nitride, which was shown to be almost complete at 1500°. Aluminium nitride, which dissociates much less readily (Fichter and Oesterheld, A., 1915, ii, 168), is oxidised by carbon dioxide at 1300° only to the extent of 89%. Briegleb and Geuther's statement may have been due to confusion of hydrocyanic acid with cyanogen, since the authors observed a transient odour of the former from the product of the action of carbon monoxide on magnesium nitride. It is suggested in explanation of this that magnesium cyanide may have been produced to a slight extent by a reaction analogous to that by which calcium nitride is converted into the cyanide by the action of carbon and nitrogen.

J. K.

**The Reactions of the Metallurgy of Zinc.** M. LEMARCHANDS (*Compt. rend.*, 1920, **170**, 805—807).—From a study of the interaction of zinc oxide and carbon in an atmosphere of nitrogen, it is shown that zinc oxide is readily reduced directly by carbon without the necessary intermediate formation of carbon monoxide. The amount of carbon entering into the reaction is intermediate between the amounts necessary for the two possible actions  $\text{ZnO} + \text{C} = \text{Zn} + \text{CO}$ ,  $2\text{ZnO} + \text{C} = 2\text{Zn} + \text{CO}_2$ . This is explained on the grounds that the reduction of zinc oxide by carbon monoxide,  $\text{ZnO} + \text{CO} = \text{Zn} + \text{CO}_2$ , takes place with a velocity superior to that of the reduction of carbon dioxide by carbon. This is possible, since the first action commences at 350°, and the second only at 400°. Further, for any given temperature, the vapour pressure of zinc oxide is much greater than that of carbon.

W. G.

**Lead Chromate.** MAX GRÖGER (*Zeitsch. anorg. Chem.*, 1919, **109**, 226—234).—When lead acetate is treated with an equi-

valent quantity of potassium chromate, a slightly basic lead chromate is precipitated, the relationship between lead oxide and chromic acid being represented by  $\text{PbO}:\text{CrO}_3::1\cdot104:1$ ; if, however, 20 c.c. of *N*-potassium chromate are added to 19 c.c. of *N*-lead acetate, a light yellow precipitate is produced which, on stirring, changes to an orange-yellow, crystalline precipitate of normal lead chromate. When 40 c.c. of *N*-lead acetate are mixed with 10 c.c. of *N*-potassium chromate, and the mixture evaporated to dryness on the water-bath and then washed with hot water, a basic lead chromate of the composition  $\text{PbO}, \text{PbCrO}_4$  is obtained. Rubbing 2 grams of normal lead chromate with 30 c.c. of *N*-potassium acetate solution, evaporating to dryness on a water-bath, and then washing with water, yields a double lead potassium chromate,  $2\text{PbCrO}_4, \text{K}_2\text{CrO}_4, \text{H}_2\text{O}$ .

J. F. S.

**Copper Silicon Alloys.** A. SANFOURCHE (*Rev. Met.*, 1919, 16, 246—256; from *Chem. Zentr.*, 1920, i, 409).—The alloys were prepared from electrolytic copper containing only 0.00007% of iron, and crystalline silicon, which after treatment with nitric and hydrofluoric acids left only 0.52% of residue and was free from iron; in spite of this, however, the alloys contained iron derived from the tubes, which seldom exceeded 0.25% in amount. The preparation of the alloys, the analytical methods, and the apparatus are shortly described, whilst the phase diagram and the results of microscopical and chemical investigation of the alloys are fully discussed. Rudolfi (A., 1907, ii, 352) has attributed the observed maximum (12.10% Si) to the formation of a compound,  $\text{Cu}_3\text{Si}$  ( $\text{Cu}=87.04\%$ ,  $\text{Si}=12.96\%$ ), but the difference in the silicon content exceeds the experimental error, whilst, also, the accuracy of his curve is greatly affected by the small number of alloys investigated. The formula  $\text{Cu}_{13}\text{Si}_4$  ( $\text{Cu}=87.91\%$ ,  $\text{Si}=12.09\%$ ), on the other hand, is in good agreement with the results obtained. The effect of this compound and of Rudolfi's substance,  $\text{Cu}_{10}\text{Si}_4$ , on the formation of  $\beta$ - and  $\gamma$ -crystals is considered in the light of the phase diagram, and the possibility of the assumption of solid solutions instead of definite compounds is discussed. Since it is impossible to alloy more than 12.10% of silicon with copper, all the formulæ of copper-silicon alloys requiring a higher silicon content are to be deleted from the literature.

H. W.

**Amalgams.** GIOVANNA MAYR (*Nuovo Cim.*, 1920, [vi], 19, i, 116—128).—The authoress gives a brief summary of previous work on the constitution of amalgams, and from the results of her own experiments, not described in detail, the following conclusions are drawn. When the chemical constitution of an amalgam is known, determination of the *E.M.F.* of a concentration cell furnishes a means of deducing the ratio between the concentrations of the two amalgams forming the cell. During the passage of a current through an amalgam, the metal dissolved in the mercury is transported towards the anode, that is, in the direction of the negative current. As regards such transport, no appreciable distinction is

evident (1) between metals, such as thallium, which give rise to compounds with the mercury, and those, such as zinc, which dissolve as such in mercury, or (2) between metals, such as sodium and potassium, which increase the resistance of the mercury, and those, such as zinc, which diminish the resistance. Thus, in contradiction to Lewis's view (compare Lewis, Adams, and Lanman, A., 1916, ii, 76), such transport of the metal does not appear to be related to the increase or decrease of the resistance of the mercury produced by dissolution of the metal. Increase in the resistance of mercury may depend on the specific resistance of mercurides formed by the dissolved metal. T. H. P.

**Colourless Variety of Mercuric Iodide.** G. TAMMANN (*Zeitsch. anorg. Chem.*, 1920, **109**, 213—214).—A colourless variety of mercuric iodide may be obtained as follows: a quantity (10—15 grams) of mercuric iodide is placed in a long tube, sealed at one end and connected with a large vessel at the other, and heated at 300—350°. The pressure is suddenly reduced to 0.1 atm., when mercuric iodide condenses in the large vessel as a white snow, which in a few seconds becomes rose-coloured, and in a few minutes has changed to the stable vermilion form of mercuric iodide. If the large vessel is previously cooled, the white form may be preserved for longer periods. The yellow variety of mercuric iodide becomes colourless at the temperature of liquid air. J. F. S.

**The Solubility of Mercuric Oxide in Sodium Hydroxide Solutions.** G. FUSEYA (*J. Amer. Chem. Soc.*, 1920, **42**, 368—371).—To determine whether a compound can possibly be formed through the interaction of mercuric oxide and sodium hydroxide, solubility determinations of the former were made in sodium hydroxide solutions of different concentrations at 25°. The solubility curves, in which concentration of mercuric oxide is plotted against sodium hydroxide and hydroxyl-ion concentrations, respectively, when extrapolated to zero concentration of hydroxide or hydroxyl ion, give a value for the solubility of mercuric oxide considerably above the normal solubility in pure water. It is considered probable that the normal solubility is that of the red form of the oxide, whilst the extrapolated value represents that of the more finely divided yellow form. The steady increase of the solubility of mercuric oxide as the concentration of sodium hydroxide increases indicates that the hydrated oxide functions as a very weak acid. The ionisation constant of the first hydrogen of mercuric acid,  $\text{H}_2\text{HgO}_2$ , is calculated to be  $1.7 \times 10^{-15}$ . E. H. R.

**Scandium.** II. JAN STĚRBA-BÖHM (*Bull. Soc. chim.*, 1920, [iv], **27**, 185—195. Compare A., 1914, ii, 565).—A study of scandium fluoride and certain of its double salts. Scandium fluoride, as prepared by Crookes's method (compare A., 1908, ii, 695), is not pure, because of the absorption of impurities during the precipitation. The fluoride may be obtained in a pure state



by the action of hydrofluoric acid on scandium oxide, the product being finally heated at 150—180° to remove any free hydrogen fluoride. Fluoroscandic acids do not exist in the free state, but three ammonium scandifluorides were prepared. The ammonium scandifluoride,  $(\text{NH}_4)_3\text{ScF}_6$  (compare Meyer, A., 1914, ii, 369), undergoes hydrolysis in water, giving first the compound,  $(\text{NH}_4)_2\text{ScF}_5$ , quadratic crystals, and then the compound,  $(\text{NH}_4)\text{ScF}_4$ , as a microcrystalline powder. The first compound is only obtained by hydrolysis in the presence of ammonium fluoride; in warm or cold water alone the second compound is always obtained.

A small quantity of a crystalline *silver scandifluoride* was obtained by dissolving scandium fluoride in a concentrated solution of silver fluoride.  
W. G.

**Light Reactions of Cerium Dioxide.** CARL RENZ (*Zeitsch. anorg. Chem.*, 1920, **110**, 104—106).—Pure cerium dioxide, which has a pale yellow colour, is unaffected by light, but if mixed with a small quantity of praseodymia or terbina it becomes light-sensitive. Such a mixture, which has a slightly reddish-yellow colour, when exposed to sunlight becomes bluish-grey, but in the dark its original colour is restored. In the cerite earths, cerium is known to have an oxidising influence on praseodymia, and apparently in sunlight this influence becomes emphasised. Discussing the position of the rare earth metals in the periodic system of the elements, the author expresses the view that, in the building up of the system, these elements are the counterpart of the transition members of the radioactive series in the degradation of the system.  
E. H. R.

**The Rare Earths. X. The Purification and Atomic Weight of Samarium.** A. W. OWENS, C. W. BALKE, and H. C. KREMERS (*J. Amer. Chem. Soc.*, 1920, **42**, 515—522).—The samarium material used for these experiments was obtained from the Welsbach Mantle Co., and consisted of rare earth residues from monazite sand after extraction of most of the cerium. The cerium remaining was first removed by treatment of the nitrates with bromine. Lanthanum, praseodymium, and neodymium were removed by fractionation of the rare earth magnesium double nitrates, first from aqueous solution and then from nitric acid. Europium and gadolinium were removed by fractionation of the rare earth magnesium nitrates with bismuth magnesium nitrate, the samarium material used for the atomic weight determinations being taken from the middle series of the last fractionations. The final purification consisted in the alternate precipitation of the samarium material as hydroxide and oxalate, and five recrystallisations as hydrated chloride. Attempts to determine the atomic weight from the oxide-chloride ratio were abandoned, owing to the impossibility of obtaining pure oxide. The ratio hydrated chloride-anhydrous chloride was also found unsatisfactory, because of the difficulty of obtaining pure samarium chloride hexahydrate.

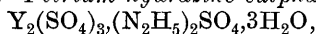
Finally, the anhydrous chloride-silver ratio was used, by determining the weight of silver, as nitrate, needed to precipitate the whole of the chlorine from a known weight of anhydrous samarium chloride, the end-point being determined by means of the nephelometer. A mean of eighteen determinations gave 150.43 as the atomic weight of samarium (Ag, 107.88), the extremes being 150.40 and 150.49.

E. H. R.

**Gadolinium. Methods of Separation of the Terbium and Ytterbium Earths.** R. J. MEYER and ULRICH MÜLLER (*Zeitsch. anorg. Chem.*, 1919, **109**, 1—30).—A number of methods of separating gadolinium from the rare earths occurring in euxenite have been examined and the efficiency of the separations compared. The alkali double sulphate method is only of use for separating a mixture which contains gadolinium into two parts, one of which contains the whole of the gadolinium. The hydrazine double sulphate method effects separation in the same way as the alkali double sulphate method, but it has the advantage of being more easily controlled. Fractional crystallisation of the bromates effects an extremely good separation of the terbium earths from the ytterbium earths, but the cerium earths cannot be separated from the terbium earths because the solubility of gadolinium bromate lies between that of samarium and neodymium bromate. Consequently, this method must be used along with another to bring about the required separation. The fractional crystallisation of the acetates effects a rapid separation of gadolinium from samarium and didymium. The great value of this method lies in the fact that it is the complement of the bromate method, and an alternation of these with the double nitrate method, which fractionates in the opposite direction, brings about a good separation. Crystallisation of the formates fractionates in the same sense as the bromates, so that a combination of the formate and acetate methods is capable of yielding pure terbium earths. Crystallisation of the double manganese nitrates, whilst very good for the separation of the cerium and yttrium earths, is found to be of very little use in separating a small amount of cerium earths from a large amount of gadolinium. Bismuth double nitrates, however, will effect this separation, and by this means a specimen of very pure gadolinium oxide was prepared. Crystallisation of the nitrates effects a fairly rapid separation of the cerium earths from gadolinium, but towards the end of the fractionation the separation becomes incomplete. The method is far inferior both in ease of manipulation and in efficiency to the acetate method. Gadolinium and terbium are easily separated by the fractional precipitation with ammonia.

The following hydrazine rare earth double sulphates have been prepared and are described: *Lanthanum hydrazine sulphate*,  $\text{La}_2(\text{SO}_4)_3 \cdot (\text{N}_2\text{H}_5)_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ , separates in sparingly soluble, colourless crystals on warming a solution of the mixed sulphates to 75°. *Neodymium hydrazine sulphate*,  $\text{Nd}_2(\text{SO}_4)_3 \cdot (\text{N}_2\text{H}_5)_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ , is formed in reddish-violet crystals, which separate on warming a

solution of the mixed sulphates. *Gadolinium hydrazine sulphate*,  $\text{Gd}_2(\text{SO}_4)_3 \cdot (\text{N}_2\text{H}_5)_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ , separates in colourless, sparingly soluble crystals when a solution of the mixed sulphate is boiled for a considerable time. *Yttrium hydrazine sulphate*,



is prepared by concentrating a solution of the mixed sulphates until crystallisation takes place. It is very soluble in water. *Scandium hydrazine sulphate*,  $\text{Sc}_2(\text{SO}_4)_3 \cdot 3(\text{N}_2\text{H}_5)_2\text{SO}_4$ , is a very soluble compound which forms good crystals.

The solubility of several acetates of the rare earths has been determined in water; the following values, in grams per 100 grams of saturated solution at  $25^\circ$ , are given: lanthanum, 14.47; praseodymium, 21.48; neodymium, 20.76; samarium, 13.05; gadolinium, 10.37; and yttrium, 8.28. The best starting materials for the preparation of gadolinium compounds are: euxenite, samarskite, or the monazite residues, but in any case the preparation should be commenced with several kilos of material.

The following method of procedure is recommended for the purification of gadolinium compounds: (1) If the rare earth mixture contains little cerium earths and much yttrium earths the gadolinium is separated with the cerium earths in one operation by the potassium double sulphate method. (2) If the mixture contains much cerium earths the major portion of these is separated by the double nitrate method. In either case a fraction very much richer in gadolinium is obtained. This is converted into the bromates and the yttrium earths removed by fractionation. Hereby the ytterbium earths first pass into the mother liquors, then follow the erbium earths, and last of all yttrium. It is essential that the yttrium should be removed at this point, for it is scarcely possible to separate it at any of the succeeding stages. The main fraction contains samarium, gadolinium, neodymium, terbium, and europium; it is converted into acetate and fractionated, the fractionation being combined with the fractionation of the double bismuth nitrates. The cerium earths are rapidly separated, and a brown mixture of oxides, containing gadolinium and terbium, is obtained. These two elements are rapidly separated by fractional precipitation with ammonia. It is possible, by the above method, to obtain pure gadolinium oxide in a few months.

J. F. S.

**Ammonia Derivatives of the Haloids of Bivalent Manganese and Iron.** WILHELM BILTZ and GUSTAV F. HÜTTIG (*Zeitsch. anorg. Chem.*, 1919, 109, 89—110).—The ammonia derivatives of ferrous and manganous chloride, bromide, and iodide have been investigated, some new derivatives have been prepared, and the dissociation pressure and curves of the various products have been determined for a number of temperatures. Anhydrous manganous chloride rapidly absorbs ammonia at the temperature of solid carbon dioxide and alcohol to form the hexa-ammine,  $\text{MnCl}_2 \cdot 6\text{NH}_3$ , which is a pure white compound. At  $76.5^\circ$  the isothermal falls a little and then remains horizontal until the com-

position falls to that of the diamine, where the pressure falls suddenly to the value for this compound. The isothermal for the equilibrium  $\text{MnCl}_2 \cdot 2\text{NH}_3 \rightleftharpoons \text{MnCl}_2 \cdot \text{NH}_3 + \text{NH}_3 \rightleftharpoons \text{MnCl}_2 + 2\text{NH}_3$  has been determined at  $229^\circ$ , and indicates the existence of the monammine. No other amines of manganous chloride exist in equilibrium with ammonia in the temperature and pressure range examined. The following dissociation pressures ( $p$ ) and heat of dissociation ( $Q$ ) have been calculated from the experimental results: hexammine,  $59^\circ$ ,  $p=218$  mm.;  $63^\circ$ ,  $p=258$  mm.;  $76.5^\circ$ ,  $p=495$  mm.;  $Q=12.6K$  (mean); diammine,  $181^\circ$ ,  $p=65$  mm.,  $Q=18.7K$ ;  $206^\circ$ ,  $p=196$  mm.,  $Q=18.8K$ ;  $230^\circ$ ,  $p=407$  mm.,  $Q=19.1K$ ; monammine,  $215^\circ$ ,  $p=9.4$  mm.,  $Q=22.1K$ ;  $230^\circ$ ,  $p=28$  mm.,  $Q=21.75K$ ;  $278^\circ$ ,  $p=95$  mm.,  $Q=22.7K$ . Manganous bromide forms similar amines to the chloride; the following values have been calculated from the isothermals: hexammine,  $107^\circ$ ,  $p=305$  mm.,  $Q=14.26K$ ; diammine,  $182^\circ$ ,  $p=13.7$  mm.,  $Q=20.2K$ ;  $215^\circ$ ,  $p=56.4$  mm.,  $Q=20.4K$ ;  $230^\circ$ ,  $p=98.0$  mm.,  $Q=20.5K$ . In the case of manganous iodide, the hexammine and diammine alone exist; the isothermals indicate the non-existence of a monammine; the following values are calculated: hexammine,  $154^\circ$ ,  $p=316$  mm.,  $Q=16.2K$ ; diammine,  $208^\circ$ ,  $p=11.1$  mm.,  $Q=21.6K$ ;  $215^\circ$ ,  $p=14.6$  mm.,  $Q=21.7K$ . By similar dissociation experiments ferrous chloride is shown to form a monammine in addition to the hexammine and diammine already known. The following values for the ferrous chloride amines are obtained: hexammine,  $90^\circ$ ,  $p=270$  mm.,  $Q=13.65K$ ; diammine,  $230^\circ$ ,  $p=121$  mm.,  $Q=20.3K$ ;  $277^\circ$ ,  $p=555$  mm.,  $Q=20.7K$ ; monammine,  $214.5^\circ$ ,  $p=5.8$  mm.,  $Q=22.5K$ ;  $277^\circ$ ,  $p=54.4$  mm.,  $Q=23.1K$ . Ferrous chloride also forms a pure white, voluminous compound with six molecules of methylamine and a grey compound with two molecules of methylamine. Ferrous bromide absorbs ammonia rapidly at ordinary temperatures to form a white hexammine, which dissociates at elevated temperatures into a dirty white diammine, and this into a dark grey monammine. The following data are calculated from the isotherms: hexammine,  $107^\circ$ ,  $p=126$  mm.,  $Q=14.9K$ ; diammine,  $215^\circ$ ,  $p=11.5$  mm.,  $Q=21.9K$ ;  $230^\circ$ ,  $p=23.5$  mm.,  $Q=21.9K$ ;  $277^\circ$ ,  $p=126$  mm.,  $Q=22.3K$ ; monammine,  $215^\circ$ ,  $p=5.7$  mm.,  $Q=22.6K$ ;  $230^\circ$ ,  $p=9.7$  mm.,  $Q=22.8K$ ;  $277^\circ$ ,  $p=61.5$  mm.,  $Q=23.1K$ . In the case of ferrous iodide a monammine does not exist; the following values are obtained for the other two amines: hexammine,  $153^\circ$ ,  $p=206$  mm.,  $Q=16.5K$ ; diammine,  $215^\circ$ ,  $p=6.1$  mm.,  $Q=22.5K$ ;  $231^\circ$ ,  $p=12.1$  mm.,  $Q=22.6K$ ; and  $278^\circ$ ,  $p=85.4$  mm.,  $Q=22.8K$ . All the measurements and calculated values are compared with those of Ephraim (A., 1912, ii, 546; 1914, i, 17; 1913, ii, 129) and Girardet (A., 1911, ii, 43).

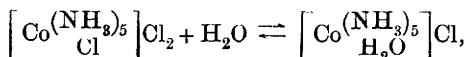
J. F. S.

**Non-rusting Iron.** HANNS FISCHER (*Chem. Zeit.*, 1920, **44**, 242).—A discussion on the ancient pillar of Northern India which, after 3000 years, is quite free from rust. A satisfactory explanation of the phenomenon is not yet forthcoming.

E. H. R.

**Cobaltammines.** NIL RATAN DHAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 576—579. Compare A., 1913, ii, 319; 1914, ii, 57).—The preparation of cobaltammines is guided by the law of mass action, and thus depends on the concentration of the reacting substances. A nitro-group in a compound may be replaced by an amino-group by warming the compound with a mixture of ammonium hydroxide and an ammonium salt, whilst the reverse change is brought about when the salt is warmed with a nitrite solution.

The hydrolysis of purpureo-cobalt chloride to give aquopentamminecobalt chloride,

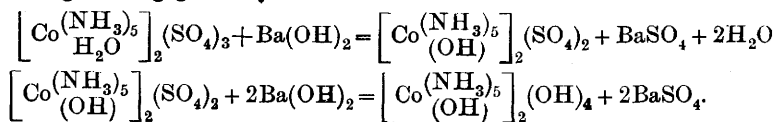


is catalytically accelerated by the presence of hydroxyl ions.

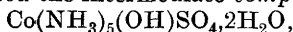
The hydroxides of the cobaltammines may be prepared in solution by treating the corresponding haloid with moist silver oxide, but purpureo-cobalt chloride under these conditions gives aquopentamminecobalt hydroxide.

W. G.

**The Constitution of Two Cobaltammines.** PAUL JOB (*Compt. rend.*, 1920, **170**, 731—734).—Titration of roseo-cobaltic sulphate by barium hydroxide, the action being followed by electrical conductivity measurements, shows that the action takes place in two stages. The curve has two singular points, the first corresponding with the precipitation of one-third of the sulphuric acid and the second with its complete precipitation. These results support Werner's view as to the constitution of the roseo-cobalt salts, the changes being given by



The author has isolated the intermediate compound,

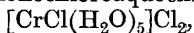


in a crystalline form.

In the same way diroseo-cobalt sulphate when titrated with barium hydroxide gives a singular point when two-thirds of the sulphuric acid is precipitated, and another when the whole of it is precipitated.

W. G.

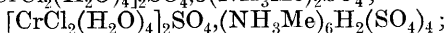
**Green Double Salts of Chromium Chlorides.** NILS LARSSON (*Zeitsch. anorg. Chem.*, 1920, **110**, 153—165).—A number of new double salts formed by monochloroaquochromium chloride,



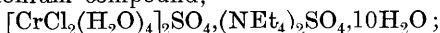
and dichloroaquochromium chloride,  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}$ , with chlorides and sulphates of different bases have been prepared. The double salts correspond in colour with the simple chromium compounds, the dichloro-compounds being light green and the monochloro-compounds light bluish-green. The compounds of the former class

are more hygroscopic, and, in general, less readily soluble than those of the latter. In all the compounds described containing the sulphate radicle, the whole of this radicle is precipitated by barium nitrate, and is therefore outside the complex chromium radicle. The following compounds were prepared.

*Double Salts with Sulphates.*—(1) Dichlorochromi-compounds:  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}_2, 2(\text{NH}_4)_2\text{SO}_4, 2\text{H}_2\text{O}$ ;  $[\text{CrCl}_2(\text{H}_2\text{O})_4]_2\text{SO}_4, 3(\text{NH}_4)_2\text{SO}_4$ ;  $[\text{CrCl}_2(\text{H}_2\text{O})_4]_2\text{SO}_4, (\text{NH}_4)_6\text{H}_2(\text{SO}_4)_4$ ; tetramethylammonium compound,  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{SO}_4, (\text{NMe}_4)_2\text{SO}_4, 3\text{H}_2\text{O}$ ; methylammonium compounds,  $[\text{CrCl}_2(\text{H}_2\text{O})_4]_2\text{SO}_4, 3(\text{NH}_3\text{Me})_2\text{SO}_4$ ;

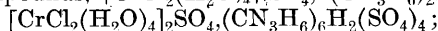


tetraethylammonium compound,



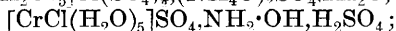
ethylammonium compound,  $[\text{CrCl}_2(\text{H}_2\text{O})_4]_2\text{SO}_4, (\text{NH}_3\text{Et})_2\text{SO}_4, 6\text{H}_2\text{O}$ ;

guanidine compounds,  $[\text{CrCl}_2(\text{H}_2\text{O})_4]_2\text{SO}_4, 3(\text{CN}_3\text{H}_6)_2\text{SO}_4$ ;



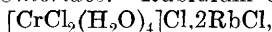
pyridine compound,  $[\text{CrCl}_2(\text{H}_2\text{O})_4]_2\text{SO}_4, (\text{C}_5\text{NH}_6)_2\text{SO}_4, 4\text{H}_2\text{O}$ .

(2) Monochlorochromium compounds: ammonium compounds,  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2, (\text{NH}_4)_2\text{SO}_4, \text{H}_2\text{O}$ ,  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{SO}_4, (\text{NH}_4)_2\text{SO}_4$ ;  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{SO}_4, (\text{NH}_4)\text{HSO}_4$ ; methylammonium compound,  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{SO}_4, (\text{NH}_3\text{Me})_2\text{SO}_4$ ; dimethylammonium compound,  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{SO}_4, (\text{NH}_3\text{Me}_2)_2\text{SO}_4$ ; tetramethylammonium compound,  $2[\text{CrCl}(\text{H}_2\text{O})_5]\text{SO}_4, (\text{NMe}_4)_2\text{SO}_4$ ; ethylammonium compound,  $2[\text{CrCl}(\text{H}_2\text{O})_5]\text{SO}_4, (\text{NH}_3\text{Et})_2\text{SO}_4, 4\text{H}_2\text{O}$ ; hydroxylamine compounds,  $2[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}(\text{SO}_4)_2, (\text{NH}_4\text{O})_2\text{SO}_4, 2\text{H}_2\text{O}$ , and



pyridine compound,  $2[\text{CrCl}(\text{H}_2\text{O})_5]\text{SO}_4, (\text{C}_5\text{H}_6\text{N})_2\text{SO}_4$ ; strychnine compound,  $2[\text{CrCl}(\text{H}_2\text{O})_5]\text{SO}_4, (\text{C}_{21}\text{H}_{22}\text{N}_4\text{O}_2)_2\text{SO}_4$ .

*Double Salts with Chlorides.*—Rubidium compound,



stable in air, heated at  $85^\circ$ , loses three molecular proportions of water and changes into Neuman's salt,  $[\text{CrCl}_5(\text{H}_2\text{O})]\text{Rb}_2$ ; ammonium compound,  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2, \text{NH}_4\text{Cl}, \text{H}_2\text{O}$ ; rubidium compound,  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2, \text{RbCl}$ ; caesium compound,  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2, \text{CsCl}$ . No potassium salt could be prepared, but a very hygroscopic lithium salt was obtained.

E. H. R.

**Chromi-aquo-triammines.** FR. FROWEIN (*Zeitsch. anorg. Chem.*, 1920, **110**, 107—124).—Conductivity measurements have been made on the three compounds, dichloromonaquotriammin-chromichloride,  $[\text{Cr}(\text{NH}_3)_3\text{Cl}_2, \text{H}_2\text{O}]\text{Cl}$ ; monochlorodiaquotriammin-chromichloride,  $[\text{Cr}(\text{NH}_3)_3\text{Cl}(\text{H}_2\text{O})_2]\text{Cl}_2$ ; and triaquotriammin-chromichloride,  $[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$ . Three isomerides of the monoaquo-compound have been described by Seemann (*Inaug. Diss.*, 1910, p. 27), but, of these, only the chloride I was examined. The compounds were prepared by Seemann's methods with slight modifications. The monoaquo-compound gradually passes over in solution into the diaquo-, and this, in turn, into the triaquo-compound, and on this account it was necessary to make the conductivity measurements on the freshly prepared solutions. The

changes can be followed by the change of colour of the solution, that of the monoquo-compound being blue, that of the diaquo reddish-violet, and that of the triquo red. These changes are more rapid the more dilute the solutions. The conductivity of the monoquo-compound is lowest, that of the triquo-compound highest, so that the change is accompanied by a gradual increase in conductivity of the solution. No direct transformation of the mono- into the tri-aquo-compound occurs, but the diaquo-compound is always the first hydration product of the monoquo. It is concluded from the measurements that the compounds contain no water outside the inner sphere, that is, they are purely co-ordinated compounds. The solution of the triquo-compound undergoes slow decomposition, the conductivity curve first showing a maximum, followed by a minimum. Deposition of chromium hydroxide eventually takes place, but intermediate complex compounds are probably first formed.

E. H. R.

**Recovery of Ammonium Molybdate from Residues, etc., obtained in Estimating Phosphoric Acid by Lorenz's Method.** H. NEUBAUER and E. WOLFERTS (*Zeitsch. anal. Chem.*, 1919, **58**, 445—448).—The filtrates, precipitates, etc., obtained in Lorenz's method (A., 1901, ii, 278) are partially neutralised with ammonia, and the molybdic acid is precipitated at 80° by the addition of an excess of sodium phosphate; the yellow precipitate is collected, dissolved in ammonia, the phosphoric acid precipitated by the addition of magnesium nitrate, the precipitate removed, and the filtrate concentrated. Ammonium molybdate crystallises out, and is purified by recrystallisation, first from very dilute ammonia solution, and then from water.

W. P. S.

**The Uranyl Radicle as a Chromophore.** ARNO MÜLLER (*Zeitsch. anorg. Chem.*, 1919, **109**, 235—274).—The colour of a large number of uranyl salts is considered; the colour is, in general, yellow, but the presence of hydroxyl or keto-groups, particularly in the  $\alpha$ - or ortho-positions, displaces the colour strongly towards the red. The benzene nucleus also acts strongly in displacing the colour towards the red end of the spectrum, particularly when the uranyl group is directly connected with phenolic oxygen. The author has tabulated the formulæ, crystal system, melting point, solubility in water, alcohol, and ether, and colour of fifty-five monocarboxylic, dicarboxylic, hydroxy-carboxylic, phenolcarboxylic, and polycarboxylic acid salts of the uranyl group. The method of preparation and the properties of fifty-two uranyl salts of aromatic and aliphatic acids of various types are described.

J. F. S.

**Some Compounds of Zirconium and the Hydrolysis of its Salts.** ED. CHAUVENET (*Ann. Chim.*, 1920, [ix], **13**, 59—86).—A résumé of work already published (compare A., 1914, i, 321; 1917, ii, 264, 321, 322, 374, 416; 1918, ii, 234, 269, 321).

W. G.

**Alloys of Gold and Silicon.** CLARA DI CAPUA (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 111—114).—Warren (A., 1893, ii, 474) and Vigouroux (A., 1896, ii, 600) have shown that gold forms an alloy with silicon. The author has studied the diagram of state of the system gold, of 0.999 purity and silicon containing 4—5% of impurity, mostly iron, being used. Fusion and cooling of the mixtures were carried out in a rapid current of hydrogen. Owing to the low thermal conductivity of silicon, the duration of the arrests of the cooling was very irregular, and yielded no information. The cooling results show that gold and silicon are miscible in all proportions in the liquid condition, that they form no compounds, and that they are non-miscible in the solid state, at any rate within the limits of the experimental accuracy attained. The eutectic alloy melts at 370°. With the alloy containing 85% of silicon, no retardation corresponding with the solidification of the eutectic is observable, but microscopic examination reveals crystals of gold scattered throughout the mass; the formation of mixed crystals at this concentration is therefore excluded. Almost all the alloys rich in silicon exhibit at the surface a golden-yellow globule, which is sharply detached from the greyish-blue, metallic block, and contains a greater proportion of gold than the mixture from which it is formed. A similar globule has been observed with silicon-silver alloys (compare Arrivaut, A., 1908, ii, 1035) and with silicon-aluminium alloys (compare Fraenkel, A., 1908, ii, 592), and its formation is certainly due to the fact that silicon solidifies with increase of volume. Hence, during the solidification, the part which solidifies last, namely, the eutectic, is forced upwards and forms the globule.

The melting point of gold is lowered by about 800° by 6—7% of silicon.

Microscopic examination of the alloys fully confirms the results of the thermal analysis.

T. H. P.

**Ammonium Pentahalogenoruthenates.** A. GUTBIER (*Zeitsch. anorg. Chem.*, 1919, **109**, 187—212).—Polemical. A criticism of statements as to ruthenium and its double chlorides in a paper by Mylius and Mazzucchelli (A., 1915, ii, 491), in which it is shown that the method of preparation of ammonium pentachlororuthenate suggested by these authors is not capable of giving this compound. [See also Gutbier and Trenkner, A., 1905, ii, 463.]

J. F. S.

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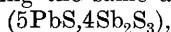


## Mineralogical Chemistry.

**Bismutoplagonite, a New Mineral.** EARL V. SHANNON (*Amer. J. Sci.*, 1920, [iv], **49**, 166—168).—A lead-grey, indistinctly fibrous mineral associated with pyrites, quartz, etc., was sent from Wickes, Montana. The streak is dark brownish-grey; D 5.35, H 2.8. The mineral is completely soluble in hot concentrated hydrochloric acid, whilst the pyrites is only slightly attacked. In the analysis (I), the sulphur was estimated by difference, the iron being assumed to represent pyrites; the insoluble portion also consisted mainly of pyrites. Deducting these impurities, the recalculated composition II agrees with the formula  $5\text{PbS}, 4\text{Bi}_2\text{S}_3$ , in which a small amount of the bismuth is replaced by antimony.

	PbS.	FeS <sub>2</sub> .	Sb <sub>2</sub> S <sub>3</sub> .	Bi <sub>2</sub> S <sub>3</sub> .	Insoluble.	As <sub>2</sub> S <sub>3</sub> , CuS, Ag <sub>2</sub> S.	Total.
I.	30.21	1.25	3.37	45.62	18.88	traces	99.33
II.	38.13	—	4.26	57.61	—	—	100.00

The ratio  $\text{PbS}:\text{R}_2\text{S}_3$  being the same as in plagonite,



the mineral is placed in the plagonite group, together with liveingite ( $5\text{PbS}, 4\text{As}_2\text{S}_3$ ), rather than with galenobismutite ( $\text{PbS}, \text{Bi}_2\text{S}_3$ ).

L. J. S.

**Hæmatite and Rutile formed by the Action of Chlorine at High Temperatures.** H. E. MERWIN and J. C. HOSTETTER (*Amer. Min.*, 1919, **4**, 126—127).—In the course of experiments on the removal of iron from clay pots by leading chlorine into the covered pots, heated in a gas-fired furnace at 1000—1100°, when they were removed from the furnace directly after the chlorine treatment, a deposit of hæmatite crystals was found on the outer, upper portion of the pot where chlorine and vaporised ferric chloride had come into contact with the products of combustion of the furnace. The crystals were in the form of rhombohedra with perfect faces. On the inside of one of the pots were found crystals of rutile in the form of very thin, twinned plates. The formation of crystals of hæmatite and rutile from vapours containing ferric chloride or titanium chloride has been previously recorded.

E. H. R.

**Calcite from New York State.** H. F. GARDNER (*Amer. Min.*, 1920, **5**, 3—5).—Enormous crystals (180 kilos.) of calcite of a dull lavender or violet colour were obtained from a cave in a limestone quarry at Sterlingbush, Lewis Co., N.Y. These have been grouped as a cave in the New York State Museum at Albany, and by transmitted lamp light show a deep rose-red to light pink colour. They

contain Fe 0.08, Mn 0.12, Mg 0.09, corresponding with  $\text{FeCO}_3$  0.17,  $\text{MnCO}_3$  0.25,  $\text{MgCO}_3$  0.32. Neodymium, to which the colour is attributed (A., 1917, ii, 209), is present in amounts too small for analytical recognition.

L. J. S.

**Latent Heat of Fusion of Cristobalite.** E. W. WASHBURN (*J. Amer. Ceram. Soc.*, 1919, 2, 1007—1008).—The author assumes that, in binary systems containing some alumina and a large proportion of silica, the solute exists in the form of molecules having simple molecular weights, and calculates the latent heat of fusion of cristobalite by means of the law regulating the lowering of the fusion point of dilute solutions, using the formula  $L = RT^2/\Delta t \cdot x$ , where  $L$  = the latent heat of fusion,  $R$  = the gas constant (2 cal.),  $T$  = the absolute melting point of cristobalite (1983° abs.) (1610° is the melting point of the eutectic for binary mixtures of alumina and silica containing 87 per cent. of silica and 13 per cent. of alumina),  $t$  = the lowering of the freezing point (1710—1610°), and  $x$  = the molar fraction of the solute.

Assuming the solute is sillimanite,  $\text{Al}_2\text{SiO}_5$ ,  $L$  = 6950 cal. per mol. : on the less probable assumption that the solute is alumina,  $\text{Al}_2\text{O}_3$ ,  $L$  = 6360 cal. per mol. Giving greater weight to the former assumption, the author suggests that the latent heat of fusion of cristobalite is 6800 cal. per mol. If the molecules of the solute are associated, and so ought to be represented by layer integers in the formulæ, the heat of fusion obtained by calculation in this manner is too large.

A. B. S.

**Fusion and Transition Phenomena of Spodumene.** F. MEISSNER (*Zeitsch. anorg. Chem.*, 1920, 110, 187—195).—The transition from  $\alpha$ - to  $\beta$ -spodumene proceeds rapidly when the mineral is heated above 1000°. Experiments were made with the object of determining whether the transition is reversible. The spodumene was first heated for one and a-half hours at 900° to start the change into the  $\beta$ -form, and then samples, of varying degrees of fineness, were heated for varying periods at temperatures from 800° to 900°, the course of change being followed by density determinations. In every case the change into the  $\beta$ -form proceeded, no evidence of reversibility being obtained. The transition could be detected by optical means, in the case of thin cleavage plates, after heating for three hours at 720°, that is, 150° lower than the minimum temperature at which a change of density can be detected. In agreement with the work of Ballo and Dittler (A., 1912, ii, 758), no evidence of reversibility could be detected by thermal methods. The so-called  $\gamma$ -form of spodumene, which crystallises from the molten material, has been examined and compared with the  $\beta$ -form. In all probability the two forms are identical. The refractive indices are not appreciably different, and the difference between the melting points observed by the above authors (1380° for the  $\beta$ -form and 1290° for the  $\gamma$ -form) is probably due to the low fusion and crystallisation velocity of the substance.

E. H. R.

**Echellite, A New Mineral.** N. L. BOWEN (*Amer. Min.*, 1920, 5, 1—3).—This occurs as small, white, spheroidal masses of radiating fibres in a basic igneous rock at the Sextant portage, Abitibi river, northern Ontario. The optical characters point to orthorhombic symmetry;  $\alpha=1.530$ ,  $\beta=1.533$ ,  $\gamma=1.545$ ; positive. It is easily decomposed by hydrochloric acid. Analysis:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	BaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.
34.5	40.0	7.2	nil	4.1	trace	14.4	100.2

gives the formula  $(\text{Ca}, \text{Na}_2)\text{O}, 2\text{Al}_2\text{O}_3, 3\text{SiO}_2, 4\text{H}_2\text{O}$ . The name *echellite* (from French, *échelle*, ladder) alludes to the stepped ratios, 1, 2, 3, 4, in this formula. The ratio  $\text{CaO}:\text{Na}_2\text{O}=2:1$ . The mineral shows certain resemblances to the zeolites, but in the latter the ratio  $\text{Al}_2\text{O}_3:(\text{Ca}, \text{Na}_2)\text{O}$  is nearly always 1:1. The formula is written in the form  $(\text{Ca}, \text{Na}_2)\text{Al}(\text{OH})_2\text{Al}_2(\text{SiO}_4)_3, 3\text{H}_2\text{O}$  to show a relation to zoisite.

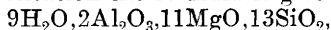
L. J. S.

**Zebedassite, a New Hydrated Silicate of Aluminium and Magnesium from Zebedassi in the Pavian Apennines.**

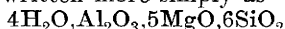
AMALIA BRUSONI (*Rend. R. Ist. Lombardo Sci. Lett.*, 1917, [ii], 50, 646—650; *Riv. Min. Crist. Ital.*, 1918, 50, 74—79).—The mineral fills fissures in an altered rock found as loose blocks on a hill of serpentine at Zebedassi, near Volpedo. The rock (partial anal. I) has probably been derived from granite or gneiss. The new mineral forms white, fibrous aggregates with silky lustre. The fibres have straight optical extinction, and are probably orthorhombic;  $n=1.51$ — $1.53$ , D 2.194, H 2. The mineral is easily soluble in acids with separation of gelatinous silica. Some water is lost over sulphuric acid, and between 105° and about 200° the loss is 2.40%. Analysis II of material dried at 105°:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	H <sub>2</sub> O (over 105°).	Total.
I. 47.06	9.80	8.09	0.82	23.58	9.01	—
II. 50.27	12.90	—	—	26.98	10.49	100.64

In the earlier publication the formula is given as



but in the later it is written more simply as



or  $\text{H}_8\text{Al}_2\text{Mg}_5(\text{SiO}_4)_6$ . The mineral is near neolite.

L. J. S.

## Analytical Chemistry.

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**Analytical Weighing.** HORACE L. WELLS (*J. Amer. Chem. Soc.*, 1920, **42**, 411—419).—The author advocates the use of the short swing method of weighing in place of the more tedious long swing method so often advocated in text-books.

E. H. R.

**A Nephelometer.** CHARLES CHÉNEVEAU and RENÉ AUDUBERT (*Compt. rend.*, 1920, **170**, 728—731).—The construction of the nephelometer is based on the formula  $I/I_0 = 1 - e^{-B/M^3}$ , where  $I$  and  $I_0$  are the intensity of the transmitted and incident light respectively and  $M$  the total mass of the particles in suspension in the medium. The absorption of the medium is compensated by a prism of very slight angle, of neutral tinted glass. It is shown that the displacement,  $x$ , of this prism for the compensation is a linear function of  $M$ , and consequently the value of  $M$  may be read off directly on a scale. [See, further, *J. Soc. Chem. Ind.*, 1920, 350A.]

W. G.

**Machine for Washing Precipitates.** ERIC SINKINSON (*Analyst*, 1920, **45**, 94—97).—The funnel containing the filter and precipitate to be washed is supported in a ring at one end of a counterpoised rocking arm; the latter is connected with a commutator to reverse a motor actuating the valve on the water supply. When the motor is started, the valve is opened and water is admitted through a rotating jet on to the precipitate. As soon as a certain weight of water has collected in the funnel, the rocking arm is depressed, the motor is reversed, and the valve closed. As soon as a sufficient quantity of water has passed from the funnel, the rocking arm rises, the motor is thus again reversed, and water admitted to the funnel, and so on.

W. P. S.

**New, Simple and Rapid Process for Collecting and Characterising the Films Produced by Metalloids and Metals capable of being Volatilised by Heat.** AD. BRALY (*Compt. rend.*, 1920, **170**, 661—663).—A simple portable apparatus is described for use in the field by prospectors in the examination of minerals. It consists essentially of two plates of mica, suitably mounted, on one of which the mineral is heated in the blowpipe flame, the second being so adjusted as to condense and collect the resulting volatile vapours. To the film thus obtained the usual tests, for characterising the metals present, may be applied. By suitably regulating the flame temperature it is possible to obtain successive films from the different metals or metalloids present in the mineral.

W. G.

**The Titration of Mixed Acids by Conductivity Methods.** I. M. KOLTHOFF (*Rec. trav. chim.*, 1920, **39**, 280—302).—For the most part, the results confirm the work of Meerburg (compare A.,

1919, ii, 518). It is not possible to estimate lactic acid in gastric juice by the conductivity method, although the total acidity of the juice may be readily determined by this method.

The method is suitable for estimating, with a very fair degree of accuracy, either small amounts of weak acids, such as acetic acid, mixed with larger amounts of strong acids, such as hydrochloric acid, or vice versa, and may be applied, therefore, to the estimation of mineral acids in vinegar. Weak bases may similarly be estimated in the presence of strong bases by the conductivity titration method.

W. G.

**A Simple, Rapid Method for the Estimation of Halogen in Organic Substances.**

W. A. VAN WINKLE and G. McP. SMITH (*J. Amer. Chem. Soc.*, 1920, **42**, 333—347).—A simple and accurate combustion method has been developed for the estimation of chlorine, bromine, or iodine in readily volatile organic compounds. The weighed material is volatilised with air from a specially designed sample holder, and is passed through a quartz tube heated for a length of about 25 cm. at 900—1000°. The products of combustion pass to an absorption apparatus containing an absorbing solution, prepared by mixing 25 c.c. of 5*N*-sodium hydroxide solution with 10 c.c. of 2*N*-sodium sulphite solution. The sulphite serves to reduce any oxy-halogen salts formed. The time taken for the combustion is from one to two hours. The excess of sulphite in the absorbing solution is then oxidised with potassium permanganate, and the halogen estimated by the Volhard process. The method was used for the analysis of ethyl bromide, ethyl iodide, ethylene chloride, bromobenzene, allyl bromide, chloroform, chloropicrin, and a number of other compounds, and gave results equal or superior to those given by the Carius method. With a slight modification of the apparatus, equally good results were obtained for less volatile substances, such as hexachlorobenzene, *m*-chloronitrobenzene, and *p*-bromoaniline.

E. H. R.

**Detection of Chloride in the Presence of Bromide.**

CARL FAURHOLT (*K. Danske Vidensk. Medd. Math. Phys.*, 1919, **2**, No. 9, 1—16; from *Chem. Zentr.*, 1920, ii, 424).—Hager's method, which depends on the separation of the silver haloids from one another by taking advantage of their differing solubilities in ammonia and ammonium sesquicarbonate solution, is modified by the substitution of very dilute ammonia to which a little silver nitrate is added, in order to depress the solubility of silver bromide without sensibly altering that of silver chloride. Potassium nitrate is also added to prevent the possibility of the formation of colloidal solutions (0.25 mol.  $\text{NH}_3$  + 0.01 mol.  $\text{AgNO}_3$  + 0.25 mol.  $\text{KNO}_3$  or 0.50 mol.  $\text{NH}_3$  + 0.05 mol.  $\text{AgNO}_3$  + 0.25 mol.  $\text{KNO}_3$  per litre).

H. W.

**Chlorides in Water Analysis.** E. MALMEJAC (*J. Pharm. Chim.*, 1920, [vii], **21**, 263—268).—Results of analyses of various waters

are recorded, and attention is directed to the fact that the quantity of chlorine present affords a useful indication of the presence or absence of animal-polluting substances, especially when the normal chlorine content of the water is known.

W. P. S.

**Estimation of Chlorides in Whole Blood.** J. HAROLD AUSTIN and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1920, **41**, 345—348).—The protein is precipitated from the blood by picric acid, or by a mixture of picric and nitric acids. The protein-free filtrate is then treated with silver nitrate, a quantitative precipitation of the total chlorides being obtained. The final titration may be carried out by the Van Slyke-Donleavy process (*A.*, 1919, ii, 239).

J. C. D.

**The Estimation and Kinetics of Hypiodous Acid in Acid Solution.** VICTOR COFMAN (*Bull. Soc. chim.*, 1920, [iv], **27**, 234—239).—Hypiodous acid reacts almost instantaneously with phenolic compounds, giving stable iodo-compounds (compare T., 1919, **115**, 1040), and on this is based the method for estimating this acid in the presence of free iodine or other iodine compounds. To a known, suitable volume of the liquid under examination, potassium iodide is added, and, after acidifying, if necessary, the free iodine is titrated with standard thiosulphate. This operation is then repeated, but an excess of phenol is added before the potassium iodide. The difference in the amount of iodine found by these two titrations is a measure of the amount of hypiodous acid present. An examination of the reversible action  $2\text{I}_2 + \text{HIO}_3 + 2\text{H}_2\text{O} \rightleftharpoons 5\text{HIO}$  shows that the velocity of formation of hypiodous acid is that of a bimolecular reaction. Similarly, measurements of the velocity of decomposition of the acid show that this change is also bimolecular.

W. G.

**Gravimetric Analysis. XII. Estimation of Sulphuric Acid. II.** L. W. WINKLER (*Zeitsch. angew. Chem.*, 1920, **33**, 59—60).—Investigation of the precipitation of sulphuric acid as barium sulphate showed that when the acidity of the solution was reduced to *N*/100 by the addition of potassium carbonate or ammonia, the solution then boiled, treated with barium chloride solution, and the precipitate collected after eighteen hours, the weight of the precipitate, dried at 130° (about 0.3 gram), required to be multiplied by 1.0045 to obtain the correct weight. If the precipitate was ignited before being weighed, the factor was 1.0099. It was proved that the barium sulphate dried at 130° lost a small quantity of sulphuric acid when ignited. If sodium carbonate was used for the neutralisation of the sulphuric acid, the results obtained were not concordant.

W. P. S.

**The Kjeldahl Method for the Estimation of Nitrogen.** I. K. PHELPS and H. W. DAUDT (*J. Assoc. Off. Agric. Chem.*, 1919, **3**, 218—220).—By using 0.7 gram of mercuric oxide, 10 grams of potassium sulphate and 25 c.c. of sulphuric acid, with

from 0.2 to 0.4 gram of substance, it was found that the Kjeldahl method was trustworthy for the estimation of nitrogen in the following compounds: glucosamine hydrochloride, isatin, atropine, cocaine, nicotinic acid, alkaloids, including caffeine, quinoxaline hydrochloride, 2-methyl-4-quinazalone, and 3-phenyl-2-methyl-4-quinazalone. The hydrolysis required 2.5 hours. W. P. S.

**Use of Potassium Permanganate in Estimating Nitrogen by the Kjeldahl Method.** WILLIAM FREAR, WALTER THOMAS, and H. D. EDMISTON (*J. Assoc. Off. Agric. Chem.*, 1919, **3**, 220—224).—In estimating nitrogen in a number of different fertilisers, there was a considerable loss of nitrogen when permanganate was added at the end of the acid digestion period; the extent of the loss depended on the amount of permanganate added, and more particularly on the time at which the addition was made. If the addition was delayed for two minutes after the burner had been removed, there was no loss of nitrogen.

W. P. S.

**A Modification of the Apparatus for the Estimation of Arginine Nitrogen by Van Slyke's Method.** GEORGE E. HOLM (*J. Amer. Chem. Soc.*, 1920, **42**, 611—612).—A modified apparatus for the Van Slyke estimation of arginine consists of a Kjeldahl flask fitted with a cork, which carries a tap funnel for the addition of water at the end of the potassium hydroxide digestion; and the elongated, water-jacketed tube of a Kjeldahl still-head. This arrangement obviates loss of material by bumping, or of ammonia in the transference from one vessel to another, in the ordinary procedure.

J. K.

**Distillation of Ammonia.** B. S. DAVISSON (*J. Ind. Eng. Chem.*, 1920, **12**, 176—177).—For the distillation of ammonia in the estimation of nitric nitrogen (A., 1919, ii, 242), the most trustworthy results are obtained by the use of a condenser of block tin and the scrubber previously described (A., 1919, ii, 296). In using this apparatus with the ordinary Kjeldahl process, the following method of distillation removes the last traces of ammonia from the condenser without unduly increasing the volume of liquid in the receiving flask, which leads to hydrolysis of the indicator salt. The solution is slowly distilled for twenty minutes, so as to collect about 80 c.c. of distillate, the condenser then drained, and the distillation continued for another fifteen minutes. The receiver is then covered to prevent absorption of carbon dioxide, and the distillate cooled and titrated.

C. A. M.

**Volumetric Estimation of Ammonia in Blood.** P. GERARD (*Compt. rend. Soc. Biol.*, 1919, 1186; from *J. Pharm. Chim.*, 1920, [vii], **21**, 236—237).—Ten c.c. of the blood are collected in potassium oxalate solution in a test-tube 22 cm. in depth, 10 c.c. of 29% sodium carbonate solution and 2 c.c. of octyl alcohol are added (the alcohol prevents excessive frothing), and air is aspirated

through the mixture at the rate of 3 litres a minute for about seventy minutes. The test-tube is connected with an absorption vessel containing a definite quantity of  $N/100$ -sulphuric acid, which absorbs the ammonia, and the excess of acid is titrated subsequently with sodium hydroxide solution, using methyl-orange as indicator. W. P. S.

**Estimation of the Nitro-group in Aromatic Organic Compounds.** T. CALLAN, J. A. RUSSELL HENDERSON, and N. STRAFFORD (*J. Soc. Chem. Ind.*, 1920, **39**, 86—88t).—Although the nitro-group in many organic compounds may be estimated by reduction with titanium trichloride solution, the excess of the latter being titrated subsequently, in the case of  $\alpha$ -nitronaphthalene, *o*-nitroanisole, nitrotolyl methyl ether, and similarly constituted compounds, the results obtained are much too low, owing to the formation of chlorinated amines. If titanous sulphate is used in place of titanium trichloride, chlorination does not occur, and the results obtained are trustworthy. Methods involving the use of stannous chloride also possess the disadvantage that, in certain cases, chlorinated compounds are formed. A method depending on the reduction of the nitro-group with zinc and hydrochloric acid, and titration of the amine with sodium nitrite solution, yielded trustworthy results with such compounds as chloronitrobenzene-*o*-sulphonic acid, nitroanisole, *p*-nitrotoluene-sulphonic acid, etc. W. P. S.

**The Acidimetric Estimation of Boric Acid.** J. A. M. VAN LIEMPT (*Rec. trav. chim.*, 1920, **39**, 358—370).—Boric acid may be estimated electrometrically by measuring the hydrogen-ion concentration of the solution after successive additions of standard alkali, providing a suitable excess of either mannitol, glycerol, or lævulose is previously added. The volume of alkali added is plotted against the values of  $p_H$ , and the curve shows a very marked inflexion at the neutralisation point if sufficient of the polyhydric alcohol has been added. W. G.

**Estimation of Available Oxygen in Sodium Perborate and in Perborate Soap Powders.** H. TRICKETT (*Analyst*, 1920, **45**, 88—91).—Titration of the perborate with permanganate solution is not very trustworthy; the best results are obtained by adding a slight excess of the perborate solution to a definite quantity of  $N/10$ -permanganate solution acidified with sulphuric acid, and then titrating the excess with permanganate solution. The temperature of the solution should be about  $15^\circ$ , and the acidity 5% of sulphuric acid, calculated on the total volume. The gasometric method for the estimation of perborate by means of permanganate is untrustworthy. A gasometric method depending on the decomposition of the perborate with hypochlorite is described. The perborate solution is treated in a nitrometer with sodium hypochlorite solution, and the volume of oxygen measured after the mixture has been shaken for five minutes. This method



may be applied directly to perborate soap powders, and the results obtained agree with those yielded by the usual iodometric method.

W. P. S.

**Estimation of Carbon.** L. LESCŒUR (*J. Pharm. Chim.*, 1920, [vii], **21**, 257—263).—The organic substance is mixed in a covered silver crucible with a mixture consisting of equal weights of sodium nitrate and potassium nitrate, sodium hydroxide solution (free from carbonate) is added, the whole is dried, and then fused. After cooling, the mass is dissolved in water, ammonium chloride and calcium chloride are added, and the resulting calcium carbonate is collected, washed, and titrated with *N*/1-hydrochloric acid, using methyl-orange as indicator. [See, further, *J. Soc. Chem. Ind.*, 1920, May.]

W. P. S.

**Rapid Method for the Estimation of Carbon in Organic Mixtures, particularly in Urine.** L. LESCŒUR and O. DUTRIEUX (*Compt. rend. Soc. Biol.*, 1919, **82**, 1417—1418; from *Chem. Zentr.*, 1920, ii, 427).—The specimen, containing 100—200 mg. of carbon, is heated in a suitable vessel, preferably a silver crucible provided with a lid and exit tube, with an excess of sodium hydroxide (about 50 c.c. of a *N*-solution), and 10 grams of a mixture of equal amounts of potassium and sodium nitrates until vapours are no longer evolved, and finally to redness for a short time. The product is dissolved in hot water, and the alkali carbonate formed is estimated titrimetrically.

H. W.

**Combustion by the Sulphochromic Mixture of Organic Compounds containing Chlorine.** J. GUYOT and L. J. SIMON (*Compt. rend.*, 1920, **170**, 734—736).—The method of oxidation of methyl esters by a mixture of sulphuric and chromic acids (compare this vol., i, 284) has been extended to chloro-compounds with success. It is necessary to interpose between the reaction vessel and the gas burette, where the carbon dioxide is measured, an amalgamated spiral of copper to retain the chlorine. In addition, in some cases there is a tendency to form carbonyl chloride, but this can be overcome by using an excess of chromic acid.

Theoretical results were obtained with methyl chlorosulphonate and chloroformate, but in the case of the ethyl esters, the ethyl group did not readily undergo oxidation. It is of interest to note that, whereas acetic acid did not undergo oxidation by this method (*loc. cit.*), its chloro-derivatives are completely oxidised. This difference is confirmed by a comparison of the behaviour of hydrocarbons and their chloro-derivatives towards this oxidising agent.

W. G.

**Estimation of Mineral Constituents in Organic Substances, especially those containing Phosphorus.** J. GROSSFELD (*Chem. Zeit.*, 1920, **44**, 285—286).—The addition of magnesium acetate solution is recommended; after the mixture

has been dried, it is readily ignited, and the ash is free from unburnt carbon. Allowance must be made for the amount of magnesium oxide added as acetate.

W. P. S.

**Explosion during the Separation of Potassium by the Perchlorate Method.** A. F. JOSEPH and F. J. MARTIN (*J. Soc. Chem. Ind.*, 1920, **39**, 94r).—To estimate sodium in a plant ash, the potassium was separated by precipitation as perchlorate, the filtrate and alcoholic washings (containing the sodium and excess of perchloric acid) were evaporated, and the sodium estimated as sulphate. On one occasion, when the alcoholic solution had been evaporated to a volume of a few c.c., violent explosion occurred. Possibly, some non-volatile substance derived from the alcohol reacted with the concentrated perchloric acid.

W. P. S.

**Estimation of Magnesium in Blood.** W. DENIS (*J. Biol. Chem.*, 1920, **41**, 363—365).—The citrated plasma, serum, or whole blood is precipitated by three volumes of 6.5% trichloroacetic acid solution. The filtrate is used for the estimation of calcium, which is precipitated as oxalate by Lyman's method (A., 1917, ii, 271). The filtrate from the calcium is evaporated to dryness in a platinum dish with a small volume of 10% sulphuric acid and ignited over a free flame for two or three minutes. The cooled residue is dissolved in a small volume of distilled water, and the magnesium is precipitated as ammonium magnesium phosphate. An indirect estimation of the magnesium in this precipitate is then made by an estimation of the phosphate present by the nephelometric method with the strychnine molybdate reagent.

J. C. D.

**Estimation of Mercury by Glückmann's Method and Modifications of the same.** ARTHUR ABELMANN (*Zeitsch. anal. Chem.*, 1919, **58**, 443—445).—The method (compare Peters, A., 1900, ii, 576) is liable to give untrustworthy results, owing to the solubility of mercury oxalate and the formation of basic salts, but this may be prevented by the addition of 2—3 c.c. of 5*N*-nitric acid to the mercury solution, using a large excess of oxalic acid for the precipitation, and introducing 50 c.c. of saturated potassium nitrate solution before the excess of oxalic acid is titrated with permanganate.

W. P. S.

**Estimation of Mercury in Organic Compounds.** A. WÖBER (*Zeitsch. angew. Chem.*, 1920, **33**, 63—64).—The organic matter is destroyed by heating 0.5 gram of the substance with 5 c.c. of sulphuric acid in a flask fitted with a tapped funnel and a delivery tube connected with a Peligot tube cooled externally with water; 1 c.c. of concentrated hydrogen peroxide solution is added, drop by drop, through the funnel, and the heating is continued until sulphur trioxide fumes appear in the Peligot tube and a clear solution is obtained in the flask. The contents of the latter are then cooled, diluted, 1 gram of sodium chloride is added, the mix-

ture neutralised with sodium hydroxide, and, together with rinsings from the Peligot tube, diluted to 100 c.c. The mercury is estimated in this solution by the iodometric method described by Rupp (A., 1908, ii, 1073). W. P. S.

**Detection of Manganese and Zinc in the Presence of Phosphates or Oxalates.** H. WESTER (*Ber. Deut. Pharm. Ges.*, 1920, **30**, 142—145; *Pharm. Weekblad*, 1920, **51**, 381—385).—In the presence of phosphates, manganese is precipitated as phosphate when its solution is treated with ammonia or ammonium sulphide; the precipitate does not dissolve in an excess of the reagents, and ammonium chloride does not prevent the precipitation. When oxalates, but not phosphates, are present, the manganese remains in solution when treated with ammonia, etc. Zinc is not precipitated by an excess of ammonia and ammonium chloride, even in the presence of oxalates and phosphates.

W. P. S.

**Gravimetric Estimation of Manganese in Iron Ores and in the so-called Manganese Ores.** BALLOT (*Bull. Sci. Pharmacol.*, 1919, **26**, 514—516; from *Chem. Zentr.*, 1920, ii, 425).—The ore (0.25 gram, or 0.5—1 gram in the case of low manganese content) is fused with sodium peroxide in a nickel crucible. The cold, fused mass is dissolved in warm water (250 c.c.), and any manganate or permanganate is reduced by cautious addition of 95% alcohol. The filtered oxides of iron and manganese are dissolved by warming in a mixture of hydrochloric acid (10 c.c.), nitric acid (10 c.c.), and water (20 c.c.); the solution is treated with ammonia, diluted to 200 c.c., and heated to boiling. It is then treated with a suspension of barium carbonate in small quantities at a time until the supernatant liquor is no longer yellow. The precipitate is allowed to subside, and is then filtered. Excess of barium is removed from the combined filtrate and washings by means of ammonium sulphate, and the cold filtrate (which is diluted to 500—700 c.c.) is treated drop by drop with bromine until distinctly yellow in colour; ammonia is added in excess, and the mixture is heated to boiling. The precipitated manganese oxide is ignited and weighed as  $Mn_3O_4$ . H. W.

**Volumetric Estimation of Manganese.** PAUL NICOLARDOT, ANTOINE RÉGLADE, and MAX GELOSO (*Compt. rend.*, 1920, **170**, 808—810).—In using Knorre's method for the volumetric estimation of manganese, the manganese being precipitated by ammonium persulphate as the dioxide, and this precipitate redissolved in an excess of some reducing solution, which in its turn is titrated with standard permanganate, the theoretical factor for the calculation is 1 gram of iron = 0.4917 gram of manganese. In practice, it is found that this factor varies, owing to slight variation in the composition of the manganese dioxide precipitate. These variations are shown to be due to the presence of iron, the factor being 0.498 in the absence of iron and 0.4929 in the presence of 40% of iron. The acidity of the solution in which the pre-

precipitation occurs also has some influence, as when there is above 10% of sulphuric acid the precipitation of the manganese is incomplete.

W. G.

### The Gravimetric Estimation of Molybdenum as Sulphide.

JAN STĚRBA-BÖHM and JAROSLAV VOSTŘEBAL (*Zeitsch. anorg. Chem.*, 1920, **110**, 81—103).—The difficulties attending the estimation of molybdenum as sulphide can be avoided if the precipitation is carried out in presence of formic acid and certain precautions are taken. In presence of mineral acids, or even acetic or oxalic acid, precipitation is incomplete, on account of the formation of colloidal solutions. The molybdenum must all be present as molybdate, and any trace of reduced molybdenum must be first oxidised by means of nitric acid. The following procedure is recommended for carrying out a determination. A quantity of solution is taken containing from 0.1 to 0.3 gram of molybdenum trioxide, and is diluted with water to 200—300 c.c. Sufficient formic acid is then added to give a 5% solution of free acid. If less than this quantity of formic acid is used, colloidal solutions of molybdenum sulphide are liable to be formed, but more acid is not detrimental. If only small quantities of electrolytes are present in solution, it is advisable to add a small quantity of pure potassium chloride, up to 0.75%, calculated on the total volume of the solution. Directly the formic acid has been added, a rapid stream of hydrogen sulphide, free from acid, is passed through the solution, for the first half hour in the cold and then for one to one and a-half hours at 40—50°. Alternatively, the hydrogen sulphide may be passed for two hours into an alkaline solution of the molybdate (alkaline with ammonia or potassium hydroxide), the formic acid then added, and the solution heated for one hour on the water-bath. The precipitated molybdenum sulphide is washed by decantation, filtered on a Gooch crucible, and dried in a current of carbon dioxide, first at 100°, then at 250°. It is then cooled in the current of gas and weighed, since it is hygroscopic, in a weighing bottle. The product obtained when these conditions are observed is shown to have the exact composition  $\text{MoS}_3$ .

The sulphide prepared as above has a brownish-black to chocolate colour. Heated in air at 126°, it oxidises considerably, and in a current of oxygen, oxidation takes place at a lower temperature with incandescence, but complete oxidation to  $\text{MoO}_3$  is only brought about with difficulty. The freshly precipitated sulphide can be digested with cold concentrated formic acid for twenty-four hours without any appreciable quantity of molybdenum passing into solution. The most delicate test for traces of molybdenum is shown to be the stannous chloride-thiocyanate-ether test, by means of which 1 part of molybdenum in 625,000 parts of water can readily be detected.

E. H. R.

[Reactions of Osmium Tetroxide]. C. A. MITCHELL (*Analyst*, 1920, **45**, 125—127).—It was shown by Schlüttig and Neumann (*Die Eisengallustinten*, 1890, 16) that to produce a permanent

coloration with iron salts (that is, an ink) a substance must contain three hydroxyl groups in juxtaposition. The same rule applies to the colour reactions of osmium tetroxide, which yields an ink with gallotannic and gallic acids and with pyrogallol, but not with phenol or quinol. In very dilute solution osmic pyrogallate is at first violet, but almost immediately becomes greenish-blue, and when applied to paper gives a deep violet-black coloration. The reaction affords a sensitive test for osmium tetroxide, the distinctive blue coloration being obtained on adding a trace of solid pyrogallol to a solution containing a few drops of 1% osmium tetroxide solution. The vapour from boiling "osmic acid" solution will develop recent finger prints on paper, and conversely a slightly greasy finger print affords a test for osmium tetroxide, traces of organic substances left by the finger giving permanent grey to black colorations owing to the reduction of the osmium tetroxide to osmium. C. A. M.

**Estimation of Trimethylene Glycol in Distilled Glycerol (Dynamite Glycerin) and in "First Runnings."** C. A. ROJAHN (*Zeitsch. anal. Chem.*, 1919, **58**, 433—442).—The quantity of trimethylene glycol present may be calculated from the water content and specific gravity of the sample. The water is estimated by drying 2 grams of the sample on asbestos under reduced pressure over phosphoric oxide. Tables and graphs are given, and reference to these gives the percentage of trimethylene glycol directly. [See, further, *J. Soc. Chem. Ind.*, 1920, 314A] W. P. S.

**The Use of Aromatic Sulphochloroamides as Reagents.** ALBERT BERTHELOT and M. MICHEL (*Bull. Sci. Pharmacol.*, 1919, **26**, 401—407; from *Chem. Zentr.*, 1920, ii, 425—426).—Neutral or alkaline solutions of sodium *p*-toluenedisulphochloroamide (chloramine-*T*) yield characteristic colorations, particularly with polyhydroxy-phenols and other substances of phenolic nature which, to a certain extent, depend on the concentration of the solutions, the quantity of reagents, the nature of the solvent, and the temperature, and, under definite conditions, are suitable for the characterisation of the individual substances. When, for example, 1 c.c. of a cold saturated solution of chloramine-*T* (about 15%) is treated with 4 c.c. of a 10% solution of the dihydroxybenzenes, a green coloration which becomes yellow is observed with resorcinol, whilst catechol gives an amethyst and quinol a currant-red coloration, which rapidly becomes brown; the effects are still noticeable at dilutions 1:10,000, 1:50,000, and 1:1000 respectively.  $\alpha$ -Naphthol solution (1%. 4 c.c.) gives a violet shade in the cold, whilst  $\beta$ -naphthol gives no coloration in the cold, but an immediate brownish-red colour in boiling solution; the extreme dilutions are 1:50,000 and 1:100,000. Similar but less characteristic effects are produced by *p*-sulphodichloroaminobenzoic acid (halazone) in sodium carbonate solution and by *p*-toluenesulphodichloroamide (dichloramine-*T*) in dichloroethylene, which may be useful for the identification of substances insoluble in water. H. W.

**Detection and Characterisation of Dextrose in Plants by a New Biochemical Method.** EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1920, **170**, 631—635).—It has previously been shown (compare A., 1913, i, 542) that 82·6% of the dextrose in solution in 70% methyl alcohol is converted by emulsin into  $\beta$ -methyl glucoside. It is now shown that this change occurs in the presence of other sugars, such as mannose, laevulose, or arabinose, and the glucoside can be isolated in a crystalline form from the solution. This method can be used for the detection and estimation of dextrose in plants as follows. The dry plant material is extracted with boiling 80% alcohol, and the extract is evaporated to dryness. The residue is extracted with boiling ethyl acetate to remove resinous matters, and the residue is dissolved in a little water, and this solution is evaporated to dryness under reduced pressure. This final residue is dissolved in 70% methyl alcohol, and after the reducing power and rotation of the solution have been measured, emulsin is added and the liquid is left until no further change in the rotation occurs. The reducing power and rotation are again determined, and from these changes the amount of dextrose present in the original plant material can be calculated, allowing for 82·6% of it having been converted into  $\beta$ -methyl-glucoside. If required, the glucoside may be isolated from the methyl-alcoholic solution.

W. G.

**A System of Blood Analysis. Supplement I. A Simplified and Improved Method for the Estimation of Sugar.** OTTO FOLIN and HSIEN WU (*J. Biol. Chem.*, 1920, **41**, 367—374).—In the method previously described (A., 1919, ii, 308) an error due to phenols is present. The authors now describe the preparation of a modified reagent, which gives no colour with phenols, but reacts with cuprous copper in acid solution. The criticisms which have been levelled at these methods on the grounds of reoxidation are discussed, and a special type of sugar tube is described, use of which prevents this source of error. The method is now considered to be without flaw.

J. C. D.

**Double Polarisation Methods for the Estimation of Sucrose, and a Suggested New Method.** GEO. W. ROLFE and L. F. HOYT (*J. Ind. Eng. Chem.*, 1920, **12**, 250—253).—The rotatory power before inversion is determined on clarified solutions containing 3% of monochloroacetic acid, within fifteen minutes of the addition of the acid, no inversion occurring within this period at the ordinary temperature. A portion of the solution is then heated in a tightly stoppered flask for thirty minutes in boiling water, and the rotatory power is determined after the cooled solution has been kept for at least two hours. When the Ventzke sugar scale is used the sucrose is calculated by the usual Herzfeld formula with the substitution of 141·0 for the Herzfeld inversion constant. The results agree well with those obtained by the use of invertase as hydrolyst. [See also *J. Soc. Chem. Ind.*, 1920, May.]

J. H. L.

**Colorimetric Estimation of Glycogen.** R. THIEULIN (*J. Pharm. Chim.*, 1920, [vii], **21**, 91—93).—Two c.c. of the neutralised glycogen solution are treated with two drops of iodine solution (iodine 1 gram, potassium iodide 2 grams, water 20 c.c.), and the reddish-brown coloration obtained is compared with those given by known amounts of glycogen under the same conditions.

W. P. S.

**Specific Colour Reaction of Oxalates.** V. MACRI (*Boll. Chim. Farm.*, 1920, **59**, 73).—The colour reaction for oxalates described by Caron and Raquet (A., 1919, ii, 438) was published earlier by the author (A., 1917, ii, 511) as a reaction for detecting manganese salts. The author now finds that addition of an oxidising agent, such as a hypochlorite, a dichromate, or hydrogen peroxide, is unnecessary, since agitation of a solution of a manganese salt in the hot with a little alkali hydroxide causes absorption of atmospheric oxygen and formation of higher oxides of manganese, these giving the characteristic red coloration with an oxalate. The reaction does not take place in acid solutions.

T. H. P.

**Approximate Estimation of Acetone and Acetoacetic Acid when present together in Urine.** EMIL LENK and WALTHER HAHN (*Münch. med. Woch.*, 1917, **64**, 179; *Zentr. Biochem. Biophys.*, **19**, 262).—The Légal test was used for the detection of acetone and acetoacetic acid collectively and the Rimini ethylenediamine test for the detection of acetoacetic acid alone. The colours obtained in both tests diminished in intensity very rapidly. In applying the reactions the pigment solutions were diluted with water until the liquid was colourless. Strongly coloured samples of urine must first be decolorised. Directions for performing the tests, together with tabulated data, are given.

CHEMICAL ABSTRACTS.

**A New Manometric Ureometer.** PAUL BOBAY (*J. Pharm. Chim.*, 1920, [vii], **21**, 62—64).—A description is given of a new ureometer, the two principal features of which are a piston with a ground surface fitting into the base of the ureometer and the addition of a manometric tube to the graduated tube. The apparatus is figured in the original, and a detailed account of its structure and method of manipulation is given.

W. G.

**Estimation of Urea in Blood.** A. SLOSSE (*Compt. rend. soc. biol.*, 1919, **42**, 1402—1404; from *Chem. Zentr.*, 1920, ii, 427).—Comparative estimations by Folin's and the hypobromite method gave practically always discordant results. Hypobromite not only decomposes urea, but also other nitrogenous substances of the blood, uric acid, creatine, creatinine, and amino-acids, which are invariably present, and, in pathological cases, frequently in such quantity that they cannot be neglected. The errors which can arise in the calculation of Ambard's constant from such data are particularly considered.

H. W.

**New Colour Reactions of Quinine.** D. GANASSINI (*Il policlinico*, 1917, **24**, 344; *Arch. ital. biol.*, 1919, **69**, 73).—A yellow coloration, which becomes rose and finally purplish-red, is developed when a few drops of pyridine are added to a solution of quinine or of a quinine salt containing a slight excess of freshly prepared chlorine water. The colouring matter is almost insoluble in chloroform. Quinidine and euquinidine respond very feebly to the test; cinchonine and cinchonidine are inert.

The green coloration developed in the thalleoquinine test with bromine water and the minimal amount of ammonia becomes red after the addition of one or two drops of a freshly prepared 0.1% solution of potassium ferri cyanide. The colouring matter is extracted by chloroform.

CHEMICAL ABSTRACTS.

**Indican in the Liquids of Organisms and its Investigation for the Identification of Urine.** LEONE LATTES (*Arch. Farm. sper. Sci. aff.*, 1919, **28**, 5—16, 17—22).—The detection of indican (indoxyl) in a spot forms a good, practical means for identifying urine, although theoretically the reaction is not absolutely specific. The reaction answers even when the spot has undergone putrefactive and similar changes. Failure of the reaction does not, however, exclude urine, since the spot may have experienced accidental alteration, besides which some urines may be either very poor in, or quite free from, indoxyl. T. H. P.

**Estimation of Hæmoglobin by the Acid Hæmatin Method.** LOUIS BERMAN (*Arch. Intern. Med.*, 1919, **24**, 553—556).—The Sahli method is modified by the use of a standard prepared daily, the use of 0.1*N*-hydrochloric acid as a diluent throughout, and heating the test to boiling for one minute after the first matching to accelerate and complete the reaction, after which the final dilution and reading are made.

CHEMICAL ABSTRACTS.

**A Comparative Study of Various Methods for the Estimation of Hæmoglobin.** FRIEDA S. ROBSCHT (J. Biol. Chem., 1920, **41**, 209—225).—When in Sahli's method the colour tubes accompanying the instrument are used, very inaccurate results may be obtained because of the decided variance in colour density of the standard tubes, due to fading. Palmer's method (A., 1918, ii, 88) is good, provided the standard solutions are freshly prepared, whilst Newcomer's method (A., 1919, ii, 179) gives good results with the glass 0.96 mm. in thickness. With the heavier glass, 1.02 mm. in thickness, the colour match is only approximate. A method is presented which applies Palmer's procedure to Sahli's principle. The standards for this process remain unappreciably changed for eleven months.

J. C. D.

**Estimation of Methæmoglobin in Blood.** WILLIAM C. STADIE (*J. Biol. Chem.*, 1920, **41**, 237—241).—The method depends on the fact that both hæmoglobin and methæmoglobin are changed quantitatively into cyanhæmoglobin by dilute solutions of potassium



cyanide. The colour of the latter substance is a brilliant orange-red, and is very suitable for colorimetric comparison. The total amount of the hæmoglobin and methæmoglobin is estimated by this colorimetric method, whilst the hæmoglobin is determined separately from the oxygen capacity, employing Van Slyke's method for the gasometric estimation of that pigment. J. C. D.

**The Detection of Blood in Fæces.** P. N. VAN ECK (*Pharm. Weekblad*, 1920, **57**, 218—227).—A critical discussion of the methods which have been proposed. A bibliography of the subject is appended. W. S. M.

**Benzidine as Chromogen in Biological Oxidation Reactions.** M. KJÖLLERFELDT (*Pflüger's Archiv*, 1918, **172**, 318—334).—The value of benzidine hydrochloride solutions for these tests is dependent on the method of preparation, and on the age of the solution. The author recommends a *N*/200-solution of the pure hydrochloride as giving the best results. J. C. D.

**Volumetric Estimation of the Alkalinity of Blood; Influence of Protein Substances on this Estimation. Its Value.** RENÉ CLOGNE (*J. Pharm. Chim.*, 1920, [vii], **21**, 49—62).—The method recommended is as follows. Five c.c. of the blood or serum are introduced into a 50 c.c. graduated flask and diluted to 40 c.c. with a saturated solution of sodium chloride. The mixture is heated on a boiling water-bath, and to it 6 c.c. of *N*/10-nitric acid are added. After three minutes the liquid is cooled and made up to the mark with more sodium chloride solution and filtered. Forty c.c. of the filtrate are titrated with *N*/10-sodium hydroxide solution, using phenolphthalein as an indicator. The average of the results obtained from the blood of fourteen normal individuals, very slightly wounded, was an alkalinity equivalent to 3.17 grams of sodium hydroxide per litre. The average for ten men suffering from severe shock was 2.79 grams per litre, and for eight men severely wounded and suffering from gas gangrene was 2.86 grams per litre.

Further investigation showed that the results obtained depended, to a considerable extent, on the amount of *N*/10-acid added, the variations obtained being due to the presence of protein. The results obtained with a solution of egg-albumin and with blood serum indicate that the alkalinity results are probably a function of the protein present rather than of the alkaline bases. W. G.

**Apparatus for Measurement of Oxydase and Catalase Activity.** R. B. HARVEY (*J. Gen. Physiol.*, 1920, **2**, 253—254).—A description of a modified Bunzel apparatus (A., 1914, ii, 508). The source of error in the earlier forms of apparatus is a failure to absorb carbon dioxide which is produced. This error is removed in the new design by using an alkali hydroxide tube. J. C. D.

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## General and Physical Chemistry.

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**Refraction and Dispersion of Carbon Dioxide, Carbon Monoxide, and Methane.** CLIVE CUTHBERTSON and MAUDE CUTHBERTSON (*Proc. Roy. Soc.*, 1920, [A], **97**, 152—159).—The refractivities and dispersion coefficients of the three gases were determined with a Jamin refractometer. For the green mercury line ( $\lambda=5461$ ), the refractivities, reduced to  $0^\circ$  and 76 cm., were as follows: carbon dioxide, 4505; carbon monoxide, 3364; methane, 4415. In all cases, the value of  $(\mu-1) \cdot 10^7$  is given. Tables giving the dispersion are supplied. The refractions and dispersions of the carbon atom calculated from the results do not show any agreement, the figures for the relative numbers of electrons and the free frequencies being also discordant. It is concluded that the forces which control the motion of a dispersion electron in an atom are profoundly affected by the proximity of another atom in combination with it. If the two atoms are of the same element, as in the molecules of diatomic gases, a similar, but probably simpler, change occurs in such a way that the free frequencies in both atoms are originally the same and are altered to the same extent.

J. R. P.

**The Variation with Pressure of the Wave-length of the Rays of the Bands of Cyanogen.** A. PEROT (*Compt. rend.*, 1920, **170**, 988—990).—By varying the pressure from atmospheric pressure down to 2—3 cm. of mercury, it is shown that the values of  $d\lambda/\lambda$  for the bands 4197 and 3883 are  $1.8 \times 10^{-6}$  and  $1.4 \times 10^{-6}$  respectively.

W. G.

**Spectrum of Copper.** W. M. HICKS (*Phil. Mag.*, 1920, [vi], **39**, 457—481).—A theoretical paper in which the copper spectrum is treated in the same way as the spectra of silver and gold (A., 1919, ii, 441). Strong, well-defined sets are given for the orders  $m=2, 3$  in both the *S* and *D* sets and for the first order of *P*. Those for *S* (2) are in the red and in step with those of silver. The others show the Zeeman patterns proper for their respective types. These may therefore be adopted definitely as normal series lines. In the higher orders, the intensities fall off more rapidly and irregularly than usual, and there is also evidence for numerous displacements. These are apparently the cause of the low intensities and the large number of weak lines. In consequence, the determination of the *S* and *D* limits, with any exactness, from the series lines alone is rendered impossible.

J. F. S.

**Effect of Solvent on the Ultra-violet Absorption Spectrum of a Pure Substance.** F. O. RICE (*J. Amer. Chem. Soc.*, 1920, **42**, 727—735).—The effect of the solvents, water, ethyl alcohol, heptane, and chloroform, on the ultra-violet absorption spectrum

of many ketones has been investigated. It is shown that all aliphatic ketones, except acetone and methyl ethyl ketone, follow Beer's law, that is, the molecular extinction is independent of the concentration and solvent. With acetone and methyl ethyl ketone there are deviations when ionising solvents are used, due to partial disruption of the associated molecules. Kundt's rule, which states that with increasing refractivity of solvent the absorption band moves towards the red, holds good if it is regarded as a rough generalisation. When a pure substance is dissolved in an ionising solvent, the absorption centre moves towards the ultra-violet; if a pure substance is dissolved in a neutral, non-ionising solvent, the absorption centre is unaffected or moves toward the red end of the spectrum. It is probable that this is a general rule which holds for all classes of absorbing substances.

J. F. S.

**Light Absorption and Fluorescence. V. The so-called Molecular Rotational Frequencies of Water.** E. C. C. BALY (*Phil. Mag.*, 1920, [vi], **39**, 565—577. Compare A., 1916, ii, 363).—A theoretical paper in which, from the atomic frequency of oxygen,  $2.4531 \times 10^{11}$ , found by the author for this substance in sulphur dioxide (*loc. cit.*), and the measurements of Sleator (*Astrophys. J.*, 1918, **48**, 125), the author is able to calculate the central frequencies of the water absorption bands. The agreement between the calculated values and the values observed by Sleator is good, the maximum difference being  $0.0022 \mu$ , whilst the average difference is  $\pm 0.00074 \mu$ . The results obtained for the system of frequencies possessed by the molecules of sulphur dioxide and water definitely establish the existence of simple relationships between the three sets of frequencies, molecular, intramolecular, and atomic. The atomic frequencies are characteristic of the individual atoms, the molecular frequencies are characteristic of the molecule as a whole, and the intramolecular frequencies are characteristic of groups of atoms in the molecules.

J. F. S.

**Activation of Hydrogen Peroxide by Light.** HARRY A. CURTIS (*J. Amer. Chem. Soc.*, 1920, **42**, 720—724).—Solutions of aniline-green and magenta are not bleached when exposed to the light of a quartz mercury lamp, neither are they bleached by the addition of 3% hydrogen peroxide to them until the mixture is exposed to the light. The rate of bleaching of the mixtures was followed by means of a Hellige-Leitz colorimeter, and curves are given. To be sure that the bleaching in light was due to hydrogen peroxide and not to ozone, solutions of the dyes were submitted to the light while a stream of oxygen was bubbled in; there was no bleaching in this case. Hence it appears that the oxidising power of hydrogen peroxide with respect to the bleaching of dyes is increased by exposing the mixture to light of short wave-lengths.

J. F. S.

**Chemical Induction in Photographic Development. I. Induction and the Watkins Factor.** S. E. SHEPPARD and G. MEYER (*J. Amer. Chem. Soc.*, 1920, **42**, 689—700).—The Lainer

effect, acceleration of development of photographic plates by dilute solutions of iodides, has been investigated, and shown to affect chiefly organic developers of low reduction potential, such as quinol. It is also shown that the principal effect is to overcome the induction with such organic developers, consequently increasing the Watkins factor. The effect is regarded as due to the increased adsorption and complex formation between silver haloid and developer. The bearing of this on the theory of development is discussed. There is, in addition, a fogging action by dilute solutions of potassium iodide on silver bromide emulsions, which is attributed to nucleus infection of the grain. J. F. S.

**Stereoisomeric Transformations and Polymerisation of Organic Substances under the Influence of Light and their Constitution.** P. R. KÖGEL (*Photo. Korr.*, 1919, 56, 368—380; from *Chem. Zentr.*, 1920, i, 489).—The acetylene and cyanogen groups are photopolymeric. The methyl group with a double bond (ethylene group) is both photostereoisomeric and photopolymorphic. The same is true of the corresponding compounds of nitrogen. The orthoquinonoid formula is assigned to anthracene on account of its ability to undergo polymerisation. The sensitiveness of diazonium compounds to light depends on their tendency to photostereoisomeric transformation. The disposition of the chief valencies in the stereoisomeric and polymeric methyl group is the same as that in the pallidogenic methyl group.

H. W.

**Photosynthesis and the Electronic Theory.** HENRY H. DIXON and HORACE H. POOLE (*Sci. Proc. Roy. Dubl. Soc.*, 1920, 16, 63—77).—Electrical measurements made with metallic plates coated with chlorophyll in different ways and illuminated from different sources of light indicate that those wave-lengths of light which are effective in photosynthesis are unable, to any appreciable extent, to expel electrons from the leaf pigment complex, and hence cannot in this way produce ionisation or bring about reactions external to the pigment. The action apparently occurs within the molecule of the chlorophyll itself, the atomic groups of the leaf pigment entering into the action of photosynthesis and participating in the combinations and decompositions which ultimately lead to the formation of carbohydrates and the evolution of oxygen.

W. G.

**The Scattering of  $\gamma$ -Rays.** K. W. FRITZ KOHLRAUSCH (*Physikal. Zeitsch.*, 1920, 21, 193—198).—A pencil of  $\gamma$ -rays, from 0.8 gram of radium chloride, after passing through absorption screens, falls on a block of carbon, aluminium, zinc, tin, or lead as radiator at 0.5 metre distance, and the secondary  $\gamma$ -radiation at different angles  $\alpha$  with the direction of incidence is examined as regards intensity and penetrating power over a circle of 0.64 metre radius, by means of an ionisation chamber. The decrease of the hardness and intensity of the secondary  $\gamma$ -radiation with increasing

values of  $\alpha$  was confirmed. The change of hardness was shown to be due to the existence in varying proportion of two types of secondary rays,  $S_1$  and  $S_2$ , corresponding with the two types of primary,  $K_1$  and  $K_2$ . The results showed that  $S_1$  was a scattered  $K_1$  radiation of the same hardness, and that probably  $S_2$  is similarly a scattered  $K_2$  radiation. None of the  $S_1$  radiation is scattered through more than  $90^\circ$ , but the  $S_2$  radiation extends in the direction of incidence as well as in that of emergence. Tables are given showing the distribution of the intensity of the radiation over the complete circle, and the results are compared with the theory of Debye and shown to be in qualitative agreement with it, particularly as regards the asymmetry of distribution found for the radiation in the directions of incidence and emergence. The probable wave-length of the  $\gamma$ -rays is discussed in the light of these results. F. S.

**The Properties of Reinforcing Screens with respect to X-ray Spectra, and a Decomposition of the  $\beta$ -Line of the  $K$  Spectrum of Tungsten.** MAURICE DE BROGLIE (*Compt. rend.*, 1920, 170, 1053—1056).—The effect of reinforcement increases rapidly with the penetration of the rays, and the luminous excitation of the screen is thus itself dependent on the absorption band of the heavy metal (tungsten in the calcium tungstate used) which the screen contains. With a screen coated with cadmium tungstate there was no apparent selective reinforcement due to the cadmium.

Using special conditions to obtain the  $K$  spectrum of tungsten it was found that the line  $\beta_1$ ,  $\lambda=0.1844$  Ångström, was split into two components, the one with the greater wave-length being the more feeble. The difference between these two components is given by  $d\lambda=0.0007$  Ångström. W. G.

**Mass-spectra of Chemical Elements.** F. W. ASTON (*Phil. Mag.*, 1920, [vi], 39, 611—625).—A full account is given of the structure and method of operating a positive ray spectrograph, which is capable of producing a focussed positive ray spectrum (mass spectrum). The results of a provisional analysis of eleven chemical elements, hydrogen, helium, carbon, nitrogen, oxygen, neon, chlorine, argon, krypton, xenon, and mercury are summarised. These show that only five—hydrogen, helium, carbon, nitrogen, and oxygen—are “pure” elements, the others being composed of various numbers of isotopic constituents. The number of isotopes  $n$  and their masses  $m$  in order of intensity are: hydrogen,  $n=1$ ,  $m=1.008$ ; helium,  $n=1$ ,  $m=4$ ; carbon,  $n=1$ ,  $m=12$ ; nitrogen,  $n=1$ ,  $m=14$ ; oxygen,  $n=1$ ,  $m=16$ ; neon,  $n=2$ ,  $m=20$ , 22 (21); chlorine,  $n=2$ ,  $m=35$ , 37 (39); argon,  $n=(2)$ ,  $m=40$  (36); krypton,  $n=6$ ,  $m=84$ , 86, 82, 83, 80, 78; xenon,  $n=5$ ,  $m=(128$ , 131, 130, 133, 135); mercury,  $n=(5)$ ,  $m=(197—200$ , 202, 204). The values enclosed in brackets are provisional. With the exception of those due to  $H_1$ ,  $H_2$ , and  $H_3$ , all masses measured, allowing for multiple charges, are exactly whole numbers within the error of experiment ( $O=16$ ). The lines due to hydrogen indicate that the

mass of this element is greater than unity on this scale, and is in good agreement with the chemical value 1.008. J. F. S.

**The Determination of the Radioactivity of Spring Waters.** OTOMAR NÜRNBERGER (*Physikal. Zeitsch.*, 1920, **21**, 198—203).—A comparison of the different methods and instruments used by H. W. Schmidt, Engler and Sieveking, Mache and Meyer, Kohlrausch and Loewenthal, for the estimation of the radium emanation in spring waters, and the conditions to be observed to obtain trustworthy and comparable results. F. S.

**Course of the Transformation Process of Isomeric Ions.** GEORG VON HEVESY and LÁSZLÓ ZECHMEISTER (*Zeitsch. Elektrochem.*, 1920, **26**, 151—153).—It is shown by the radioactive indicator method that a dynamic equilibrium exists between bivalent and quadrivalent lead ions in glacial acetic acid solution, and in consequence it follows that electrons can pass of themselves, in certain circumstances, from one ion to an isomeric ion and also to an electrode. J. F. S.

**Ionisation and Activity of Largely Ionised Substances.** ARTHUR A. NOYES and DUNCAN A. MACINNES (*J. Amer. Chem. Soc.*, 1920, **42**, 239—245).—A theoretical paper in which the experimental results of MacInnes and Parker (A., 1915, ii, 510, 734), Ellis (A., 1916, ii, 369), and Noyes and Ellis (A., 1918, ii, 27), in connexion with the electrodes  $\text{Ag} + \text{AgCl} | \text{LiCl} | \text{LiHg} | \text{LiCl} | \text{AgCl} + \text{Ag}$  and  $\text{Hg} + \text{HgO} | \text{KOH} | \text{K}$  in  $\text{Hg} | \text{KOH} | \text{HgO} + \text{Hg}$  are discussed. It is shown that in the case of potassium chloride, lithium chloride, hydrochloric acid, and potassium hydroxide the activity coefficient decreases with increasing concentration much more rapidly than does the conductivity-viscosity ratio, the differences amounting to from 7% to 15% at  $N/10$ - and from 5% to 18% at  $N/5$ -concentration. In the case of all the substances except potassium chloride, the activity-coefficient, unlike the conductivity-viscosity ratio, passes through a pronounced minimum in the neighbourhood of  $N/5$  and afterwards increases rapidly at the higher concentrations. Even potassium chloride, according to Harned's data (A., 1918, ii, 597), has a minimum activity-coefficient about  $2N$ . The activity-coefficient even at moderate concentrations varies considerably with the nature of the substance; thus its value in  $0.5N$ -potassium chloride is 65%, lithium chloride 73%, hydrochloric acid and potassium hydroxide 77%. Thus it follows that the conductivity ratio can no longer be regarded as even an approximate measure of the activity of the ions of highly ionised substances in their mass action and thermodynamic relations. The activity varies with the concentration differently in the case of different substances and, at present, it can only be determined empirically for each substance with the aid of chemical equilibrium measurements, *E.M.F.*, and freezing-point measurements. It is also shown that the ionic activity-coefficients cannot be proportional to or mainly determined by the fraction of

the substance ionised; for this fraction could not increase with increasing concentration unless the ionising power of the medium becomes much greater at moderate concentrations, and even then it could not become greater than unity, as is actually the case with the activity-coefficient of hydrochloric acid in concentrations above  $2N$ . J. F. S.

**The Constancy of Electrical Conductivity of Gases during Chemical Reactions.** MAX TRAUTZ and FRIEDRICH AUGUST HENGLEIN (*Zeitsch. anorg. Chem.*, 1920, **110**, 237—289).—To determine whether or no ionisation occurs during chemical reactions, a number of purely gaseous reactions were studied. The apparatus used consisted essentially of a glass reaction vessel of cylindrical form containing a cylindrical condenser, both surfaces of which were of graphite or glass. The outer surface was connected by a platinum wire sealed into the wall of the reaction vessel to a high-tension battery, the inner surface similarly to a quadrant electrometer set. Preliminary experiments showed that none of the materials employed, matte glass surfaces, platinum wire, graphite or paraffin, had any appreciable influence on the velocity of the reaction  $2NO + Cl_2 \rightleftharpoons 2NOCl$ . When the reaction vessel was filled with dry air and the outer electrode connected to the high-tension battery, a small charge appeared on the inner electrode and increased gradually to a maximum value, in spite of the most careful insulation of the two electrodes. This charge, it was proved, is a result of the ionisation of the gas. It increases with increasing pressure and is greater for chlorine than for air. The ionisation of the air in the enclosed vessel was considerably greater than that which has been found by other methods for free atmospheric air.

The reactions studied were the following:  $2NO + Cl_2 \rightleftharpoons 2NOCl$ ;  $2NO + Br_2 \rightleftharpoons 2NOBr$ ;  $2HBr + Cl_2 \rightleftharpoons 2HCl + Br_2$ ;  $Cl_2 + H_2 \rightleftharpoons 2HCl$ . In no case could evidence of ionisation during the reaction be obtained. Pinkus stated (A., 1918, ii, 286) that ionisation could be detected in the case of the first reaction when chlorine was in excess. His results could not be confirmed, and were probably due to frictional electricity generated by the sudden rush of gas into the reaction vessel. It is concluded that during gaseous reactions at moderate temperatures, even when the heat of reaction is great, no free electrons are produced.

Manometric experiments were made to determine whether, when gaseous hydrogen chloride, bromide, or iodide is mixed respectively with gaseous chlorine, bromine, or iodine, any hydrogen trihaloid is formed. The results in each case were negative. E. H. R.

**Disruptive [Sparking] Potential in Carbon Dioxide at High Pressures.** C. E. GUYE and P. MERCIER (*Arch. Sci. phys. nat.*, 1920, [v], **2**, 30—49, 99—124).—The authors measured the sparking potential in carbon dioxide at high pressures with great accuracy. At atmospheric pressure, with plane electrodes

45 mm. diameter, the sparking potential for the same distance is greater in air than in carbon dioxide, although this difference appears to vanish at small distances. Exposure to ultra-violet light diminishes the potential to a greater extent in carbon dioxide than in air. The action of ultra-violet light is inappreciable at pressures greater than 10 atm. For distances from 2 to 5 mm. the potential increases linearly with the pressure up to 10 atm. For 1 mm., and especially for 0.5 mm., this relation no longer holds, although the deviations are very small. The results depend on the form of the electrodes. The results are explained by an accumulation of positive and negative ions in the vicinities of the electrodes before the spark passes. This leads to the deviation from Paschen's law at small distances, and also causes the energy of the spark to increase, giving rise to a more intense spark.

J. R. P.

### Absorption of Gases in the Electric Discharge Tube.

F. H. NEWMAN (*Proc. Physical Soc.*, 1920, **32**, 190—195. Compare A., 1914, ii, 703).—A continuation of experiments previously described (*loc. cit.*). Nitrogen is absorbed by both sodium and potassium under the influence of an unidirectional discharge in a discharge tube. The experiments were made at various pressures (8.1—1.0 mm.), and with the metals as cathode and anode respectively. In the case of sodium, it is shown that the amount of absorption is greater when it is the cathode. In the case of potassium, less gas is absorbed than with sodium. Using the liquid alloy of sodium and potassium, there was no difference in the rate of absorption when the temperature was raised from 50° to 200°, but above this temperature the rate of absorption increased very much. After the discharge had been interrupted and the alloy was heated to above 300°, there was no evolution of gas, so that in all probability moderately stable nitrides of sodium or potassium, or both, had been formed.

J. F. S.

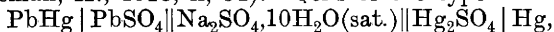
**Reproducible Liquid Junction Potentials: The Flowing Junction.** ARTHUR B. LAMB and ALFRED T. LARSON (*J. Amer. Chem. Soc.*, 1920, **42**, 229—237).—The reproducibility and constancy of liquid junction potentials has been investigated in the case of gelatin diaphragm, parchment diaphragm, and flowing junctions. The experiments show that liquid junctions formed between the bearing surfaces of ground-glass stoppers, in gelatin diaphragms, and in parchment paper diaphragms with 0.1*N*-hydrochloric acid and potassium chloride solutions are not constant and reproducible to closer than 0.2—0.4 millivolt. Somewhat more constant results are obtained with parchment diaphragms on stirring. Fresh junctions in 5 mm. tubes give potentials reproducible in 0.1*N*-solutions to about 0.03—0.06 millivolt when the electrolyte is prevented from oscillating, but with *N*-solutions variations of 0.3 millivolt occur. Stirred junctions sometimes give very constant potentials, but these are quite different from that produced by a flowing junction, and, moreover, they differ, depend-



ing on the method of stirring. A flowing junction, obtained simply by an upward current of the heavier electrolyte meeting a downward current of the lighter electrolyte in a vertical tube at its point of union with a horizontal outflow tube, or by allowing the lighter electrolyte to flow constantly into a large volume of the heavier electrolyte, even with *N*-solutions, gives potentials constant and reproducible to 0.01 millivolt. An apparatus in which such flowing junctions may be obtained is depicted in the paper.

J. F. S.

**A Lead Standard Cell.** M. G. MELLON and W. E. HENDERSON (*J. Amer. Chem. Soc.*, 1920, **42**, 676—689. Compare Henderson and Stegeman, A., 1918, ii, 54).—Cells of the type



of which the *E.M.F.* and stability have previously been studied (*loc. cit.*), were constructed, in which the electrolyte was replaced by solutions, both saturated and unsaturated, of the sulphates of potassium, lithium, magnesium, nickel, cobalt, zinc, manganese, cadmium, and copper. These cells have been examined with respect to their *E.M.F.*, reproducibility, and constancy. It is shown that the cell with sodium sulphate, constructed in 1917 (*loc. cit.*), has the same value as freshly made cells. It is shown that saturated cells containing the sulphates of nickel, cobalt, zinc, or manganese are substantially as reproducible and as constant as those containing sodium sulphate. This constancy is usually reached in four to five days after preparation, and these cells appear to possess the characteristics necessary for a standard cell. The *E.M.F.* of the cell which has become constant seems to be nearly independent of the soluble sulphate used. The value of the *E.M.F.* for cells containing sodium or nickel sulphate is practically the same, 0.96466 volt and 0.96430 volt respectively, whilst those of cells containing cobalt, zinc, and manganese sulphate are very close together, but are slightly higher than those of the first-named cells; they have values 0.96478, 0.96477, and 0.96478 volt respectively. Saturated cells containing the sulphate of lithium, magnesium, or cadmium are neither reproducible nor constant, although the *E.M.F.* has approximately the same value as the constant cells. Saturated cells containing potassium sulphate are neither reproducible nor constant; the mercurous sulphate in them is distinctly hydrolysed, and the *E.M.F.* is markedly higher than that of the other cells. Saturated cells containing copper sulphate agree well among themselves, but are not constant. The *E.M.F.* is approximately one-third that obtained for the other cells, which indicates that the lead of the amalgam replaces the copper, and a copper amalgam is produced. Unsaturated cells containing the sulphates of sodium, zinc, nickel, cobalt, and manganese are just as reproducible as the saturated cells, they have the same *E.M.F.*, and are constant for a time, and then exhibit a decreasing *E.M.F.* Unsaturated cells containing the sulphates of lithium, magnesium, and cadmium have approximately the same *E.M.F.* as the saturated cells, and they

are equally unsatisfactory. Attempts to ascertain the cause of the unsatisfactory nature of these cells were without result.

J. F. S.

**A New 0.1N-Calomel Electrode Design.** A. E. KOEHLER (*J. Biol. Chem.*, 1920, **41**, 619—620).—This type of electrode was designed to overcome the changes in normality which the solutions in other patterns of instruments are apt to show. The apparatus is illustrated, and has been used for two months without showing any change in *E.M.F.*

J. C. D.

**Platinised Glass Electrodes for Electrolytic Estimations.** G. MEILLÈRE (*J. Pharm. Chim.*, 1920, [vii], **21**, 311—313).—Electrodes suitable for many purposes may be made by fusing a small piece of platinum wire into a glass tube, watch-glass, etc., then varnishing the glass with a solution of platinum chloride and an essential oil in methyl alcohol, and heating the glass until all organic matter has been oxidised. Several successive coatings may be applied in order to obtain a suitable layer of platinum on the glass. In some cases, it is advantageous to etch the glass with hydrofluoric acid before the platinum varnish is applied.

W. P. S.

**Conduction of Electricity by Free Electrons and Carriers.**  
**III. Migration Velocity of Particles moving under Forces in Viscous Media.** P. LENARD, W. WEICK, and HANS FERD. MAYER (*Ann. Physik*, 1920, [iv], **61**, 665—741. Compare *ibid.*, 1900, 312).—A theoretical paper in which relationships are deduced for expressing and calculating the velocity of ions and other carriers of electricity in various media. Values are calculated for the radius ( $r$ ) and the number of molecules of water ( $n$ ) combined with the following ions in aqueous solution:  $H^+$ ,  $n=1.4$ ,  $r=0.9 \times 10^{-8}$  cm.;  $OH^+$ ,  $n=2.5$ ,  $r=1.4 \times 10^{-8}$  cm.;  $Li^+$ ,  $n=19$ ,  $r=5.0 \times 10^{-8}$  cm.;  $Na^+$ ,  $n=12$ ,  $r=4.2 \times 10^{-8}$  cm.;  $K^+$ ,  $n=7$ ,  $r=3.1 \times 10^{-8}$  cm.;  $Rb^+$ ,  $n=6$ ,  $r=2.9 \times 10^{-8}$  cm.;  $Cs^+$ ,  $n=6$ ,  $r=2.8 \times 10^{-8}$  cm.;  $F^+$ ,  $n=11$ ,  $r=3.9 \times 10^{-8}$  cm.;  $Cl^+$ ,  $n=6$ ,  $r=3.2 \times 10^{-8}$  cm.;  $Br^+$ ,  $n=6$ ,  $r=3.0 \times 10^{-8}$  cm.;  $I^+$ ,  $n=6$ ,  $r=2.9 \times 10^{-8}$  cm. It is shown that there is a distinct parallelism between the value of  $n$  and the temperature-coefficient of the migration velocity.

J. F. S.

**Alternating Current Electrolysis.** S. MARSH (*Proc. Roy. Soc.*, 1920, [A], **97**, 124—144).—Solutions of sulphuric acid and barium hydroxide have been electrolysed with alternating current of varying frequency by means of electrodes of gold, platinum, and nickel. In the case of platinum foil electrodes and sulphuric acid, the amount of evolution of gas decreases rapidly with time, and eventually no more gas is evolved. The amount evolved decreases with increasing frequency of the current; when thin platinum electrodes were used, the amount was less, but no simple relationship between the volume of gas evolved and the thickness

of the electrode was observed. The time-volume curves resemble the saturation curves obtained in radioactive measurements. With gold electrode and sulphuric acid, the rate of evolution of gas falls off rapidly with time, but for frequencies less than 48, gas is still given off at the electrodes for a much longer time than with platinum, and the total volumes of gas are considerably smaller than in the case of platinum. In the case of nickel, a copious evolution of hydrogen occurred for twenty minutes, beyond which the experiment could not be continued, owing to solution of the electrode. With barium hydroxide as electrolyte, the rate of evolution decreases with time and with increasing frequency, but the time-volume curves are practically straight lines. The volume of gas liberated is much greater than in acid solutions. Gold and platinum behave very similarly in barium hydroxide solution, but nickel only evolves the smallest quantity of hydrogen with a frequency of 60 cycles, and even with 40 cycles the volume of gas is too small to measure. Two suggestions are put forward to explain the phenomena: (i) the oxidation of the electrode, coupled with subsequent reduction by the hydrogen of the next half-period; (ii) the absorption and adsorption of hydrogen by the electrode, coupled with recombination with oxygen of the next half-period. These processes are not mutually exclusive, and it is possible that both agencies are operative in degrees varying with the metal employed.

J. F. S.

**Electro-endosmosis and the Preparation of Solid Alkali-metal Amalgams.** SUMNER B. FRANK and JAMES R. WITHROW (*J. Amer. Chem. Soc.*, 1920, **42**, 671—675).—A number of experiments on electro-endosmosis show that it is modified by the type of porous cell used, but that an increased voltage and current density will always cause it to take place. Using solutions of potassium chloride, potassium sulphate, strontium chloride, and calcium acetate, endosmosis is always observed if the voltage is more than 8. The phenomenon is made very visible by the following experimental arrangement. The solution, saturated by preference, is placed in a beaker fitted with any form of platinum anode, and a porous cell is immersed to a depth of about 5—10 mm. in the solution, and about 50 grams of mercury, which serves as cathode, poured in. Contact is made with the mercury in the usual way, and a voltage of 20—25 is applied. In about sixty minutes, the solution will have entered and filled the porous pot to a height of about 3—4 cm. In these experiments, solid amalgams of potassium and strontium were obtained, but in the case of calcium, no amalgam was obtained, only a mixture of calcium hydroxide and finely divided mercury.

J. F. S.

**Electrical Characteristics of Dye Colloids.** RUDOLF KELLER (*Kolloid Zeitsch.*, 1920, **26**, 173—178. Compare A., 1919, ii, 491).—A continuation of the previous discussion (*loc. cit.*), in which the reason for the discrepancy between the author's experiments and the statements of many text-books is given. It is shown

that the statement of the text-books refers to dilute solutions of dyes where the substances in solution are ion disperse systems and the coloured cation naturally travels to the cathode, whereas the author's experiments were carried out with concentrated dye solutions which were colloid disperse systems and the cation wandered in the opposite direction.

J. F. S.

**Influence of Molecular Constitution and Temperature on Magnetic Susceptibility. IV. Further Applications of the Molecular Field.** A. E. OXLEY (*Phil. Trans.*, 1920, [A], 220, 247—289. Compare A., 1914, ii, 424; 1915, ii, 219).—A theoretical paper in which the discussion previously published is continued. The applications of local molecular forcive, in diamagnetic, paramagnetic, and ferromagnetic media, have been extended to interpret the ultimate strength of crystalline and vitreous media. It is to be expected, since the permanent set which occurs prior to breaking is due to slipping along the cleavage planes within the crystal grains, that the material will be fractured when the applied mechanical stress is equal to that produced internally by the local molecular forcive. The internal stress within the material is of the order  $2 \times 10^9$  dynes per sq. cm., which is approximately the mean of the ultimate strengths of crystalline and vitreous media. As a consequence of this internal stress, the energy per unit volume will be  $2 \times 10^9$  ergs, and this energy is a measure of the latent heat of fusion per c.c. It is found that the elastic constants of a variety of ferromagnetic, diamagnetic, and paramagnetic media are of the same order, several diamagnetic and paramagnetic media even surpassing steel in their power to resist distortion. The energy change which occurs on crystallisation is compatible with a volume change of the same order of magnitude as that accompanying crystallisation, and the change of volume on crystallisation may therefore be interpreted as a magneto-striction effect of the local molecular forcive. The magneto-striction effect depends on molecular orientation, which is proportional to the square of the magnetic forcive. A physical interpretation has been given of the large values of the coefficients  $N$  and  $a_c'$  of the molecular fields in ferromagnetic and diamagnetic crystalline media respectively. These coefficients are the reciprocals of the limiting local susceptibilities of the media under field strengths equal to the respective molecular fields. The local susceptibility of a diamagnetic molecule is comparable with that of a ferromagnetic molecule, and the two vary in the same way with field strength and temperature. In diamagnetic media, however, magnetic hysteresis will be inappreciable, since the molecule as a whole possesses a zero magnetic moment. Mechanical hysteresis in diamagnetic media will be of the same order as in ferromagnetic media. It has been previously shown (*loc. cit.*) that the magneton may be a constituent of the diamagnetic hydrogen molecule. This idea may be extended to carbon and the hydrocarbons in general, where the molecular susceptibility can be directly calculated from the atomic susceptibilities of the component

atoms. The results in other cases are unconvincing, but the fact that departures from the additive law occur in these cases leads to the conclusion that some disturbing influence has been overlooked.

J. F. S.

**Magnetic Properties of Nickel-Copper Alloys.** R. GANS and A. FONSECA (*Ann. Physik*, 1920, [iv], **61**, 742—752).—The magnetic susceptibility of nickel-copper alloys has been measured over a range of concentrations from 20·3% nickel to 60·2% nickel at temperatures from  $-230^{\circ}$  to  $55^{\circ}$ , and the transformation point determined for each concentration. A series of susceptibility measurements are also given for  $15^{\circ}$  for the whole of the alloys. The results show that the Tammann rule (A., 1909, ii, 16) is not true in the present case, and that ferromagnetic substances dissolved in non-magnetic crystals yield ferromagnetic alloys. Copper-nickel alloys form a complete series of mixed crystals except over the range 45—50% nickel, in which nickel crystals saturated with copper and copper crystals saturated with nickel exist. The present results are analogous to those obtained for cobalt-copper alloys, except that in this case the gap in the mixed crystal series is considerably larger.

J. F. S.

**Magnetic Susceptibility of Antimony and Bismuth: Form of the Magnetron.**

HECTOR ISNARDI and RICHARD GANS (*Ann. Physik*, 1920, [iv], **61**, 585—590).—The specific susceptibility of bismuth and antimony has been determined by the Weiss method, using fields lying between  $H=1029$  Gauss and  $H=13680$  Gauss. The results show that the magnetic susceptibility of these metals is independent of the strength of the field, and that the apparent dependence found by Honda and Owen (A., 1910, ii, 686; 1912, ii, 425) is probably due to the presence of iron as an impurity in the material and also to errors of measurement. The following mean values are found: bismuth,  $-\chi \cdot 10^{-6} = 1.346$ ; antimony,  $-\chi \cdot 10^{-6} = 0.8138$ . From the Gans theory it is shown that the principal moments of inertia of the magneton are identical. This result is obtained only for bismuth and antimony, but judging from the measurements of Honda and Owen it is probably true for other elements.

J. F. S.

**Specific Heat of Carbon Dioxide and Steam.**

W. T. DAVID (*Phil. Mag.*, 1920, [vi], **39**, 551—553).—A theoretical paper in which the author advances the suggestion that the specific heat of steam and carbon dioxide depends not only on the temperature, but also on volume and density. At any particular temperature the greater the volume of the gas the greater its specific heat, and the greater the density the less its specific heat. In a previous communication (A., 1911, ii, 1046) the author has shown that carbon dioxide and steam emit radiation in appreciable quantity in the neighbourhood of  $1000^{\circ}$  and very strongly in the neighbourhood of  $2000^{\circ}$ . Consequently, the specific heat of these gases may be

expected to vary slightly with volume and density at 1000° and very markedly at 2000°. J. F. S.

**Secondary Valencies and Fusibility.** ARRIGO MAZZUCHELLI (*Gazzetta*, 1920, **50**, i, 93—97).—According to Nernst ("Kinetische Theorie der Materie," Leipzig, 1913), the varying fusibilities of the elements are explainable by their different numbers of primary and secondary valencies, the reciprocal attractions of which keep the atoms fixed in the crystalline network characteristic of the solid state. The author extends this conception to the interpretation of certain apparently contradictory regularities in the fusibility of metallic and non-metallic compounds.

With the latter the fusibility diminishes as the number of atoms in the molecule increases, the more complicated molecules appearing to find greater difficulty in assuming the condition of irregular movement characteristic of liquids; the same rule holds for the volatility, a measure of which is afforded by the critical temperature. The correlation between molecular complexity and melting or boiling point is most marked in homologous series of carbon compounds, and is, indeed, so general for non-metallic compounds that divergences are utilised as criteria of polymerisation in the liquid state.

With compounds of the metals, on the other hand, fusibility and volatility increase with increase in the complexity of the molecule.

To explain the different behaviour of non-metallic and metallic compounds the author advances the following considerations. From Nernst's assumption that the heavy metals are relatively infusible because their numerous primary and secondary valencies hold the atoms firmly in the crystalline network, the conclusion is drawn that combination of the metallic atom with an increasing number of oxygen or other non-metal atoms results in increasing saturation of the valencies in the interior of the molecule. Thus, the number of valencies available to maintain the molecules united in the crystalline aggregate is diminished and the fusibility consequently increased. In other words, entry of oxygen, chlorine, etc., introduces into the molecule that internal saturation of the valencies to which oxygen, chlorine, etc., owe their fusibility. This explanation applies, not only to binary compounds, but also to those of higher orders and to hydrated salts. Further, it is not invalidated by the information furnished in recent years by *X*-ray diffraction spectra, which show that the various atoms are distributed almost uniformly in the crystalline network. T. H. P.

**Apparatus for the Determination of Melting Points.** L. M. DENNIS (*J. Ind. Eng. Chem.*, 1920, **12**, 366—368).—The apparatus is similar to that described by Thiele (*A.*, 1907, ii, 330), but the lower portion is inclined downwards; the "rising" portion of the loop is of narrower diameter, and enters the main tube at an angle. It is claimed that there is better circulation of the sulphuric acid and a more uniform temperature can be maintained.

W. P. S.

**Fractionation Flask for the Distillation of Frothing Liquids.** EMIL LENK (*Chem. Zeit.*, 1920, **44**, 330).—The lower end of a condenser is fused on to the neck of an ordinary fractionating flask at a point below the outlet tube of the latter, and is then bent upwards to form a reflux condenser. These two outlets from the flask are connected with a pump, the communication being controlled by a three-way tap, so that a vacuum can be produced in either direction. In distilling a viscous liquid the reflux condenser is first exhausted, and the froth will then rise into it and the liquid subsequently fall back into the flask. When the liquid in the flask is boiling steadily a vacuum is created in the other direction and the distillation continued. To facilitate the return of substances solid at the ordinary temperature from the reflux condenser, hot water may be circulated through the cooling jacket. The inner tube of the condenser is constricted at intervals to form a series of pear-shaped bulbs. C. A. M.

**A Simple Distillation Apparatus for Separation of Water.** GEO. W. WALKER (*Chem. News*, 1920, **120**, 222).—In distilling solvents such as benzene and chloroform, which contain water, a distilling flask with two necks is used. One neck is connected by rubber tubing with a condenser, the other by rubber tubing with a flask cooled in water. At the commencement of the distillation, the tube leading to the condenser is closed by a clip, and the water allowed to distil off into the flask. The first clip is then opened, and the tube leading to the flask closed by a second clip. Distillation of the solvent then proceeds. J. R. P.

**The Energy of the Atomic Linkings in Diamond and in Aliphatic Hydrocarbons.** K. FAJANS (*Ber.*, 1920, **53**, [B], 643—665).—The heat of combustion of a saturated aliphatic hydrocarbon may be regarded as the result of the heat of formation of a carbon hydrogen bond ( $x$ ), that of a simple C—C linking in compounds ( $y$ ) [the similar linking in diamond being denoted by  $y'$ ], the heat of formation of liquid water from 1 gram atom of atomic hydrogen and molecular oxygen ( $v$ ), and the heat of formation of gaseous carbon dioxide from 1 gram atom of atomic carbon (monatomic carbon vapour) and molecular oxygen ( $z$ ). For the special cases of propane and ethane the expressions may be written:  $-8x + 8v - 2y + 3z = 526.7$  and  $-6x + 6v - y + 2z = 370.9$ , by subtraction of which there is obtained  $-2x + 2v - y + z = 155.8$  Cal. as the expression of the increase in the heat of combustion due to the addition of the methylene group. Since  $z$  and  $v$  are independent of the substance under investigation, it follows that the magnitude  $y + 2x$  is subject to but little variation, which is most simply explained by the hypothesis that  $x$  and  $y$  are constant to a first approximation, that is, the energy of a simple C—C or of a C—H linking is practically the same in different saturated aliphatic hydrocarbons. Further, an examination of the available data for various hydrocarbons leads to the conclusion that the energy of the

C-C linking in hydrocarbons is practically uninfluenced by the further attachment of the C atoms to other C or H atoms. If  $x$  and  $v$  are eliminated from the first two equations, the expression  $z - 2y = 96.5$  Cal. is obtained; the number is rather considerably influenced by slight experimental errors in the data on which it is based, but a consideration of a large number of suitable estimations leads to the equation  $z - 2y = 98 \pm 8$ . The recent work of Langmuir, Isnardi (A., 1915, ii, 738) and Franck, Knipping, and Krüger (this vol., ii, 145) allows  $v$  to be evaluated at  $74.4 \pm 2.8$  Cal. Now the heat of combustion of the diamond is the result of two factors (a) the heat required to convert solid diamond into monatomic carbon vapour [heat of sublimation], and (b) the heat of combustion of the vapour ( $z$ ) to carbon dioxide. Using Roth's values, one obtains  $z - 2y' = 94.4$  Cal. Since, however,  $z - 2y = 98 \pm 8$ , it follows that  $y' - y = 2 \pm 4$  Cal., from which it is deduced that the heat of formation of a C-C linking in saturated hydrocarbons is practically the same as that in diamond. Since  $v$  is known,  $y$  is practically equal to  $y'$ , and  $2y'$  represents the difference in energy between solid diamond and monatomic carbon vapour, the problem of dissecting the heat of formation of hydrocarbons resolves itself into the estimation of the heat of sublimation of diamond. This has been estimated by Fajans (*Zeitsch. Physik*, 1920, 1, 101) to be 287 Cal. The following values can thus be deduced:  $z = 381$  Cal.,  $y = 137.5$  Cal.,  $v = 74.4$ , and  $x = 117$  Cal. The data are applied to the calculation of the heats of formation of a series of hydrocarbons, both from diamond and hydrogen and from the atomic substances; in the latter case large positive values are always indicated, and it is interesting to note that the formation of the C=C and C $\equiv$ C linkings is associated with the development of 252 and 365 Cal. respectively, whereas the production of the C-C bond only evolves 136 Cal. Strictly speaking, it should be observed that the values assigned to the energy of the various linkings are only valid when all other available valencies of the carbon atoms are saturated.

Similar considerations are applied to the combustion of carbon in oxygen. The relatively smaller development of energy which is associated with the first stage of the oxidation is only apparent; when the heat of sublimation of diamond is taken into account, the equation may be written  $C_{\text{vapour}} + \frac{1}{2}O_2 = CO + 314$  Cal., whilst  $CO + \frac{1}{2}O_2 = CO_2 + 67.8$  Cal.

The paper concludes with a criticism of the recent communications of von Weinberg (A., 1919, i, 314) and Padoa (A., 1919, ii, 97), for details of which the original must be consulted.

H. W.

**The Energy of Atomic Linking in Graphite and in the Aromatic Hydrocarbons.** A. L. VON STEIGER (*Ber.*, 1920, 53, [B], 666—680 Compare Fajans, preceding abstract).—The investigation was undertaken with the object of referring the unique position of aromatic ring systems in organic chemistry to



the peculiar nature of their carbon atoms. It has been shown by Debye and Scherrer (A., 1917, ii, 437) from a consideration of the crystalline structure of graphite that the carbon atoms in the latter may be regarded as tervalent if the energy of the fourth bond is neglected on account of its smaller order of magnitude. Proceeding in the same manner as Fajans (*loc. cit.*), the author finds that, for purposes of calculation, the carbon atoms of purely aromatic hydrocarbons which are made up of simple or condensed six-carbon rings may be regarded as tervalent, and that all C-C linkings are equivalent. It is further found that the energy of the C-C linking in graphite is very nearly the same as in aromatic hydrocarbons. Since the molar heat of sublimation of graphite has been calculated (Fajans, *Zeitsch. Physik*, 1920, 1, 107), it is therefore possible to calculate the heat of combustion of an aromatic hydrocarbon, the constitution of which is known. It is interesting to note that the energy of the C-C and C-H groups in aromatic is greater than in aliphatic hydrocarbons, the respective values being 187.3 and 137.5 for the former and 137.7 and 117 Cal. for the latter.

Basing his ideas on the equality of energy of the C-C linking in graphite and in the purely aromatic hydrocarbons, the author traces a close analogy between the six-membered rings of the carbon planes in the former and the six-ring system of the latter, and is thus led to the following conception of the constitution of aromatic ring systems. The latter are composed of carbon atoms, which have the same disposition of valencies as the carbon atoms in graphite. The distance from one another is approximately  $1.45 \times 10^{-8}$  cm. The chief valencies lie in a plane and make an angle of  $120^\circ$  with one another. The existence of free subsidiary valencies of a smaller order of magnitude in the aromatic ring is very probable, and, if the analogy with graphite may be pushed so far, they must be considered as placed at right angles to the plane of the six-carbon ring.

H. W.

**Pressure and Temperature-coefficients, Volume, and Heat Effects in Bivariant Systems.** P. H. J. HOENEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, 22, 526—530).—A mathematical paper in which equations are developed by which the composition may be calculated of each phase of a system having  $n$  components in which there may be  $n$  co-existing phases and in which  $p$  and  $T$  are independent variables. Further equations are developed for calculating the relation between the pressure- and temperature-coefficients for the transition of the components from one phase to another in a system of  $n$  components and  $l$  phases when  $n \equiv l$ ; further expressions give the heat effects and the volume changes which accompany the transition.

J. F. S.

**Van der Waals's Force of Cohesion.** P. DEBYE (*Physikal. Zeitsch.*, 1920, 21, 178—187).—A theoretical paper in which, from a consideration of electrical attraction of two molecules for one another, expressions are derived whereby the van der Waals's constant  $b$  may be calculated. Further expressions are developed

whereby the surface tension and the Eötvös constant may be calculated. J. F. S.

**The Falling Sphere Viscosimeter.** WILLIAM HOWIESON GIBSON and LAURA MARY JACOBS (T., 1920, 117, 473—478).

**Orientation of Molecules in Surfaces, Surface Energy, Adsorption, and Surface Catalysis. V. Adhesional Work between Organic Liquids and Water.** WILLIAM D. HARKINS, GEORGE L. CLARK, and LATHROP E. ROBERTS (*J. Amer. Chem. Soc.*, 1920, 42, 700—712. Compare A., 1917, ii, 238, 239; 1916, ii, 222, 223).—A table is given which contains the free surface energy, the adhesional work per sq. cm., the interfacial free energy, the surface adhesion, and the densities of about seventy organic liquids. Of these liquids about thirty-four have been freshly investigated. The data presented are in keeping with the view that the molecules at interfaces are oriented. It is assumed from the formulæ that carbon disulphide has a symmetrical molecule and ethyl mercaptan an unsymmetrical molecule. The cohesive work is much greater in the former case than in the latter, 62·8 ergs per sq. cm. instead of 43·6, whilst the adhesional work between water and carbon disulphide is much less (55·8 ergs per sq. cm.) than it is between water and mercaptan (68·5 ergs per sq. cm.). These facts are readily explained by the orientation theory. Thus the attraction between octane and water is relatively small, the adhesional work being only 43·76 ergs. The octane molecule contains 26 atoms, and yet the introduction of one oxygen atom at the end of the chain more than doubles the adhesional work, and increases it to 91·77 ergs. A similar introduction of one oxygen atom into isopentane increases the adhesional work towards water from 36·9 to 92·5, an increase of 150%. The substitution of an amine group for a hydrogen atom at the end of a chain causes a similar increase, as also does the substitution of  $-\text{COOH}$ ,  $-\text{CN}$ ,  $=\text{CO}$ , or any similar groups. The great magnitude of the effect, when it is considered that the addition of 1 atom to 26 causes an increase of 132%, is strong evidence that the oxygen is turned towards the water. It is found that in only three cases out of fifty-eight is the cohesive work of an organic liquid greater than its adhesional work toward water. The three substances are carbon disulphide, ethylene dibromide, and acetylene tetrabromide. The excess of the adhesional over the cohesive work increases as the symmetry of the molecule decreases. This is also strong evidence in favour of the orientation theory. The benzene hydrocarbons are more polar than the paraffin hydrocarbons. Aniline is found to be extremely polar in comparison with most of the organic liquids. The polar characteristics of the benzene derivatives are distributed much more over the whole molecule than is the case with the paraffin derivatives. The total surface energy and the free surface energy are not due to the orientation of the molecules, but to the stray surface field, and this is decreased by the orientation.

J. F. S.

**Adsorption and Solubility.** E. F. LUNDELIUS (*Kolloid Zeitsch.*, 1920, **26**, 145—151).—The adsorption of iodine from solutions in carbon tetrachloride, carbon disulphide, and chloroform by blood charcoal has been determined at 19—20°. The results are plotted as absorption isotherms for the surface of 1 gram of charcoal. In general, the results show that the adsorption is inversely proportional to the solubility. The adsorption of vapours of toluene, carbon disulphide, carbon tetrachloride, chloroform, benzene, and hexane by blood charcoal has also been determined, and it is shown that approximately equal volumes of the various substances are adsorbed from their saturated vapours, from which it follows that the thickness of the layer of adsorbed material is the same in all cases examined.

J. F. S.

**Relationship between the Height of Capillary Rise, the Time, and the Concentration in the Capillary Rise in Filter Paper.** HANS SCHMIDT (*Kolloid Zeitsch.*, 1920, **26**, 152—159. Compare A., 1913, ii, 721; 1919, ii, 185).—The height to which solutions of glycerol and dextrose of various concentrations rise in filter paper has been determined at temperatures 15—17°. Also the rate of rise has been ascertained in all cases. The results show that the constant of the velocity of capillary rise is inversely proportional to the viscosity of the solution. It is also shown that it is possible, from the relationship between the time required by a given solution to rise to a definite height and that of pure water, to calculate approximately the concentration of the solution.

J. F. S.

**Cause of the Influence of Ions on the Rate of Diffusion of Water through Collodion Membranes.** I. JACQUES LOEB (*J. Gen. Physiol.*, 1920, **2**, 387—408).—In this paper it is shown that in electrical endosmose through a collodion membrane the influence of electrolytes on the rate of transport of liquids is the same as in free osmosis. Since the influence of electrolytes on the rate of transport in electrical endosmose must be ascribed to their influence on the quantity of electrical charge on the unit area of the membrane, it follows that the same explanation holds for the influence of electrolytes on the rate of transport of water into a solution through a collodion membrane in the case of free osmosis. It may, therefore, be concluded that when water is separated from a solution of an electrolyte by a collodion membrane, the rate of diffusion of water by free osmosis is accelerated by the ion with the opposite sign of charge to that of the watery phase of the double layer, and that it is retarded by ions with like charge. The influence of the ions of an electrolyte in raising or lowering the charge on the unit area of the solution side of the membrane, compared with that on the water side, will determine whether osmosis is positive or negative. A further conclusion is that in lower concentrations of many electrolytes the density of electrification of the double layer increases with an increase in concentration, whilst in

higher concentrations of the same electrolytes it decreases with an increase in concentration. In the case of a number of electrolytes the turning point lies about  $M/512$  or  $M/256$ . J. C. D.

**Extension of Braun's Law.** P. H. J. HOENEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 531—535).—A mathematical paper in which it is shown that Braun's law, which has the form  $(\partial x/\partial p)_T: (\partial x/\partial T)_p = T\Delta V/Q$ , is a particular case of a more general law which is developed in the present work. The general law is formulated thus:

$$(\partial x/\partial p)_T \cdot Qx/T + (\partial x/\partial T)_p \cdot \Delta V_x + (\partial y/\partial p)_T \cdot Qy/T + (\partial y/\partial T)_p \cdot \Delta V_y + \text{etc.} = 0,$$

in which  $(\partial x/\partial p)_T$  and  $(\partial y/\partial p)_T$  are the pressure-coefficients of the solubility of  $x$  and  $y$  respectively,  $(\partial x/\partial T)_p$  and  $(\partial y/\partial T)_p$  are the temperature-coefficients,  $\Delta V_x$  and  $\Delta V_y$  the differential increase in volume due to  $x$  and  $y$  respectively. J. F. S.

**Determination of the Dissociation Constants of some Mineral Acids.** EMILE BLANC (*J. Chim. Phys.*, 1920, **18**, 28—45).—The degree of dissociation of a number of acids and the degree of hydrolysis of the sodium salts of some of them have been determined by means of conductivity, potential, and the indicator methods. The following values for the degree of hydrolysis are found at 25° for the salts named: sodium phosphate 0.012*N* is hydrolysed 34.1%; disodium hydrogen phosphate, 0.012*N*, 0.066%; sodium phosphite, 0.0075*N*, 0.021%; sodium dihydrogen arsenite, 0.0104*N*, 0.394%; sodium arsenate, 0.002*N*, 8.0%; disodium hydrogen arsenate, 0.002*N*, 0.0455%; sodium selenite, 0.0108*N*, 0.379%; sodium hydrogen tellurite 0.0075*N*, 0.0022%; sodium tellurite, 0.0075*N*, 0.773%; sodium hydrogen tellurate, 0.0093*N*, 0.117%; sodium tellurate, 0.0093*N*, 13.97%; potassium molybdate, 0.00975*N*, 0.359%; and potassium tungstate, 0.0162*N*, 0.011%. The following new dissociation constants have been calculated from the experimental results: phosphorous acid,  $K_2 = 2 \times 10^{-5}$ ; arsenic acid,  $K_2 = 4 \times 10^{-5}$ ;  $K_3 = 6 \times 10^{-10}$ ; selenious acid,  $K_1 = 2 \times 10^{-3}$ ,  $K_2 = 5 \times 10^{-8}$ ; tellurous acid,  $K_1 = 2 \times 10^{-3}$ ,  $K_2 = 1 \times 10^{-8}$ ; telluric acid,  $K_1 = 6 \times 10^{-7}$ ,  $K_2 = 4 \times 10^{-11}$ . J. F. S.

**A Model for Demonstrating Crystal Structure.** HERBERT P. WHITLOCK (*Amer. J. Sci.*, 1920, [iv], **49**, 259—264).—The model, which is used for demonstrating the spatial distribution of the atoms in a crystal as revealed by the X-ray method of Bragg, consists of a number of thin glass rods mounted vertically in a double diaphragm perforated with holes arranged in a symmetrical pattern, a centred square pattern, for instance, for cubic, tetragonal, and orthorhombic crystals, or an equilateral triangular pattern for hexagonal and rhombohedral crystals. The atoms are represented by spherical wooden beads bored with a hole to fit the rods. The beads are spaced accurately on the rods to represent different groupings of atoms, and are fastened in position by a drop of glue.

Beads of different colours are used to represent different kinds of atom.  
E. H. R.

### **Differentiation between Molecular and Colloidal Solutions.**

WA. OSTWALD (*Kolloid Zeitsch.*, 1920, **26**, 138—140).—It is suggested that molecular and colloidal solutions may be differentiated by an examination of the ice produced by freezing them. In the colloidal solutions it is suggested that a difference in composition of successive horizontal layers may be found, due to the settling of the colloidal particles during the freezing.  
J. F. S.

### **Automatic Sedimentation Recorder and its Use in some Colloid-chemical Problems.**

SVEN ODÉN (*Kolloid Zeitsch.*, 1920, **26**, 100—121).—An apparatus is described whereby the rate of sedimentation of a suspension may be automatically recorded. The apparatus consists of a thin gold-plated disk, which is suspended to one arm of a sensitive balance and hangs inside a cylinder of nearly the same diameter in which the suspension is placed. The precipitation plate is exactly balanced by weights on the other pan, and when a small quantity of the suspended matter falls on it, it sinks; this operates an electric contact, which by means of relays causes a small iron pellet to be thrown on the weight pan. The precipitation plate is thus raised, and the contact broken. Each time the two pans are of exactly the same weight a mark is made on a slowly rotating paper coil which marks the time. Thus the weight and time, and consequently the rate of sedimentation, are known. This apparatus has been used in determining the mean and actual diameter of suspensoid particles in the case of silver bromide, the aggregation time, and the dependence of the aggregation time on the concentration of the particles and the electrolyte concentration.  
J. F. S.

### **Coagulating Power of some Electrolytes.** (MLLE.) N.

BACH (*J. Chim. Phys.*, 1920, **18**, 46—64).—The relative coagulating power of ions of the alkali metals and the halogens has been determined by means of a new method, which consists in measuring the opacity number of the electrolyte. The opacity number is the number of c.c. of a normal solution of the electrolyte which will produce a definite turbidity in a colloidal solution. This quantity can be determined with great precision, and consequently the method is well suited to this purpose. The coagulating power of an electrolyte is the reciprocal of the opacity number. It is shown that the ratio of the opacity numbers of two electrolytes depends only on the nature of the colloid, and it may be that it is even independent of this. The opacity numbers are all referred to that of potassium chloride as unity. It is found that the coagulating power of the alkali ions follows the order:  $\text{Cs}^+ > \text{Rb}^+ > \text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$  and the halogen ions  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ . Other things being equal, an alkali ion coagulates a negative colloid more powerfully and protects a positive colloid more effectually the more electro-positive it is, and a halogen ion coagulates a positive colloid and

protects a negative colloid more strongly the more electronegative it is. The coagulating power is always much more marked than the protecting power. In the case of the halogen ions the difference between the discharge potentials is proportional to the difference between the coagulating power. The coagulating power of potassium chloride mixed with hydrochloric acid, potassium hydroxide, barium chloride, potassium sulphate, lanthanum chloride, sodium citrate, and potassium ferrocyanide has also been measured, and it is shown that both the coagulating power and the protecting power are additive. It is also shown that colloidal solutions are extremely sensitive to traces of multivalent impurities. J. F. S.

**Direct Experimental Determination of the Concentration of Potassium and Sodium Ions in Soap Solutions and Gels.** CYRIL SEBASTIAN SALMON (T., 1920, 117, 530—542).

**Emulsions. I. A New Method of Determining the Inversion of Phases.** SHANTI SWARUPA BHATNAGAR (T., 1920, 117, 542—552).

**Non-, Uni-, and Bi-variant Equilibria. XX.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, 22, 542—554. Compare A., 1917, ii, 454; this vol., ii, 169).—A further theoretical paper dealing with the conditions of equilibrium in non-variant, uni-variant, and bi-variant systems. The present paper deals with the equilibria of  $n$  components in  $n$  phases, in which the quantity of one of the components approaches the zero value, and the influence of a new substance on a non-variant ( $P$  or  $T$ ) equilibrium. J. F. S.

**Equilibrium Conditions of the Reaction between Silver Sulphide and Hydrogen.** F. G. KEYES and W. A. FELSING (*J. Amer. Chem. Soc.*, 1920, 42, 246—251).—The equilibrium  $\text{Ag}_2\text{S} + \text{H}_2 \rightleftharpoons 2\text{Ag} + \text{H}_2\text{S}$  has been investigated at the temperatures  $750^\circ$ ,  $811^\circ$ , and  $890^\circ$  absolute, by the method and with the apparatus previously described by Keyes (A., 1912, ii, 627). The following values of the equilibrium constant were obtained:  $749.15^\circ$ ,  $K=0.359$ ;  $811.25^\circ$ ,  $K=0.325$ ; and  $889.63^\circ$ ,  $K=0.278$ . From the results it is shown that the heat of the reaction is to be expressed  $\text{Ag}_2\text{S} + \text{H}_2 = 2\text{Ag} + \text{H}_2\text{S} + 2410$  cal. The equilibrium constant, between  $750^\circ$  and  $890^\circ$  absolute, is expressed as a function of the temperature by means of the expression  $\log_{10} K = 525.8/T - 1.1470$ . The corresponding expression for the decrease in free energy over the same temperature range is  $-\Delta F = RT \log_e K = 2408 - 5.253T$ . J. F. S.

**Heterogeneous Equilibria between Aqueous and Metallic Solutions. Interaction of Mixed Salt Solutions and Liquid Amalgams. VI. Ionisation Relations of Sodium and Potassium Chlorides, Bromides, and Iodides in Mixtures.** L. S. WELLS and G. McP. SMITH (*J. Amer. Chem. Soc.*, 1920, 42, 185—205. Compare A., 1918, ii, 67; 1917, ii, 455).—The equilibrium between sodium and potassium amalgams and

mixtures of sodium and potassium chloride, bromide, and iodide respectively, has been investigated. It is shown that at a fixed total salt concentration the value of the equilibrium constant  $C_c = nk = (K_{Hg})(NaX)/(Na_{Hg})(KX)$  decreases with increasing concentration of the amalgam. At fixed amalgam and total salt concentrations, but with varying salt ratio, the value of  $C_c$  is constant. At a fixed amalgam concentration the value of  $C_c$  decreases with the increasing concentration of the mixed (equivalent) salt solution. Ion-fraction calculations are put forward for aqueous binary salt mixtures containing the salts in equivalent proportions. It is found that the simple potassium-ion fraction decreases, whilst the sodium-ion fraction correspondingly increases with the increasing total salt concentration. These changes take place the more rapidly the higher the average atomic weight of the halogens in the mixture. These results are not in keeping with the view that at equivalent concentration salts of the same type are ionised to the same extent. The general results of the work are readily explained in terms of Werner's theory concerning the formation and dissociation of higher order compounds. J. F. S.

**Rate of Corrosion of Aluminium.** GEORGE HERBERT BAILEY (*J. Soc. Chem. Ind.*, 1920, **39**, 118—120T).—A measure of the extent to which a sample of aluminium is corroded, in terms of the metal so corroded per day per 100 sq. cm. of surface, is given by  $CR = 9/8(S + w - W)$ , where  $W$  is the weight of the sheet employed,  $w$  its weight after exposure, and  $S$  the weight of the precipitate obtained after ignition. The variation of  $CR$  with the concentration of the corrosive solution employed at  $12^\circ$  is shown by a number of curves in which  $\log CR$  is plotted against concentration. In the case of sodium, potassium, and barium hydroxides the curves are straight lines showing increasing attack as the concentration increases, whereas the ammonia curve rises to a maximum and then falls off. For the mineral acids,  $CR$  is fairly steady up to  $0.30N$ ; in the case of hydrochloric acid the curve then rises very steeply, whilst the curves for nitric and sulphuric acids rise more gradually to maximum values and then fall. At ordinary temperatures corrosion ceases, for example, in the case of sodium hydroxide or hydrochloric acid, when the solution has become exhausted, but at higher temperatures, in the neighbourhood of  $100^\circ$ , attack continues indefinitely, with formation, in the case of hydrochloric acid, of colloidal basic salts. The formation of a protective coating causes the rate of attack to fall off considerably with time, more rapidly in the case of impure metal than with purer specimens. The protective film, in the case of ammonia, is only about  $0.01$  mm. in thickness, but it has considerable insulating power for high-tension electric currents. E. H. R.

**The Reversible Reaction between Iron and Steam.** E. SCHREINER and F. B. GRIMNES (*Zeitsch. anorg. Chem.*, 1920, **110**, 311—334).—Measurements of the equilibrium pressures of water-vapour and hydrogen in the reaction  $Fe + H_2O \rightleftharpoons FeO + H_2$  were

made between  $595^{\circ}$  and  $920^{\circ}$ , using an apparatus similar to that first employed by Deville (*Compt. rend.*, 1870, **70**, 1105, 1205). It was shown that refinements in the apparatus introduced by other workers with the object of accelerating the diffusion of the gases in the reaction tube were unnecessary. The values obtained for  $K = p_{\text{H}_2\text{O}}/p_{\text{H}}$  were in good agreement, starting from either side of the equilibrium position. There are considerable discrepancies between the results obtained by different workers, particularly at high temperatures, where, in all cases, the value of  $K$  is much lower than that calculated from thermodynamic principles. The discrepancies are probably due to reactions in the solid phase, for example, the formation of solid solutions between iron and ferrous oxide, or to the different behaviour of different modifications of iron. Further experiments are suggested to test this hypothesis.

E. H. R.

**The Influence of the Solvent on the Velocity of Reaction between certain Alkyl Iodides and Sodium  $\beta$ -Naphthoxide.**  
HENRY EDWARD COX (*T.*, 1920, **117**, 493—510).

**Hydration as an Explanation of the Neutral Salt Effect.**  
ARTHUR JOHN WILSON (*J. Amer. Chem. Soc.*, 1920, **42**, 715—720).—The addition of 120 grams of sodium chloride to chrome tanning liquor (17 grams of  $\text{Cr}_2\text{O}_3$  as sulphate per litre) increases the hydrogen-ion concentration about 50% and prevents the liquor from tanning skins. Other experiments show that the amount of 0.1*N*-sodium hydroxide necessary to produce a precipitate of basic chromic salts increases if certain neutral salts are added to the liquor, thus: 10 c.c. of the untreated liquor required 3.7 c.c., but the addition of 0.04 gram of sodium chloride increased the amount to 6.8 c.c. Using many salts the order of increase in the amount of sodium hydroxide required increases with the salts, potassium chloride (4.0 c.c.) < ammonium chloride < sodium chloride < magnesium chloride < magnesium sulphate < sodium sulphate < ammonium sulphate (11.6 c.c.). The author attributes this action to the hydration of the added salt with consequent increase of the acid concentration, and he calculates the number of molecules of water combined with one molecule of the salt in the case of sodium chloride for a number of dilutions; the following values are given: 4*N*, 10.9; 3*N*, 13.2; 2*N*, 16.3; *N*, 20.5; *N*/10, 25.5; *N*/100, 26.1; *N*/1000, 26.2; infinite dilution, 26.2. The hydrations of all the salts used are calculated for infinite dilution, and the following values obtained: potassium chloride, 15; ammonium chloride, 15; lithium chloride, 35; barium chloride, 50. J. F. S.

**The Action of Finely Divided Gases.** C. ZENGHELIS (*Compt. rend.*, 1920, **170**, 883—885).—The author attributes the action of gases in the nascent state to the fact that they are in an extremely finely divided state. This explanation is based on the fact that he has been able to obtain numerous reductions, such as of solutions of mercuric chloride, potassium chlorate, or potassium



nitrate, or of a saturated aqueous solution of carbon dioxide, by passing hydrogen, generated in an external vessel, into the liquid through filter-paper or dialysis parchment. Under somewhat similar conditions he has performed certain oxidations and brought about the combination of nitrogen and hydrogen in the cold. The reactions are, of course, slower under these conditions than when the nascent gases are used, because the state of division is probably not so fine.

W. G.

**Catalysis. XIII. Contact Potentials and Dielectric Capacities of Metals, in Relation to the Occlusion of Hydrogen, and Hydrogenation.** WILLIAM CUDMORE McCULLAGH LEWIS (T., 1920, 117, 623—638).

**Catalytic Oxidation at Solid Surfaces: Some Factors Controlling the Rate of Hydrogenation of Ethylenic Compounds in Presence of Nickel.** E. FRANKLAND ARMSTRONG and T. P. HILDITCH (*J. Soc. Chem. Ind.*, 1920, 39, 120—124T).—The hydrogenation of ethyl cinnamate and of anethole in presence of nickel at 140° and 180° takes place at practically a linear rate throughout the greater part of its course, when a free current of hydrogen is maintained. When, however, the reaction is carried out in a closed system, the rate gradually falls off and the curve approximates to the logarithmic type. This is due solely to the decreasing concentration of the hydrogen, caused by the gradual accumulation of gaseous impurities from the hydrogen and, to a less extent, from the organic compound. The results confirm the authors' previous conclusions drawn from a study of the hydrogenation of olive, cottonseed, linseed, and whale oils (A., 1919, ii, 403; this vol., ii, 102). The hydrogenation of anethole gives rise to a crystalline by-product which has not been identified, but ethyl cinnamate is reduced quantitatively to ethyl  $\beta$ -phenylpropionate.

E. H. R.

**Catalytic Hydrogenation with Protected Hydrosols.** ERIC K. RIDEAL (*J. Amer. Chem. Soc.*, 1920, 42, 749—756).—The effect of a protective colloid on the reaction velocity of a hydrogenation process in the presence of colloidal platinum and palladium has been studied, and the results lead to the conclusion that the protecting colloid functions as a peptising agent, in agreement with Bancroft's hypothesis (A., 1917, ii, 129). The addition of a small quantity of a palladium sol to a platinum sol greatly enhances its activity, and it is suggested that promoter action may in part be due to peptisation. The mechanism of catalytic actions in the presence of colloidal metal appears to conform rather to the diffusion hypothesis than to the colloid reactant complex theory. Abnormalities are equally explicable on the single-layer theory as on the view that the retardation of diffusion is caused by the products of the reaction. The various reactions were studied by means of the influence of the colloidal metals on solutions of sodium phenylpropionate in the presence of gum arabic.

J. F. S.

**Rhythmic Mercury-Hydrogen Peroxide Catalysis.**

TOKIHARU OKAYA (*Proc. Phys. Math. Soc. Japan*, 1919, [iii], 1, 283—294).—The theory deduced by the author in connexion with the rhythmic precipitation of silver chromate in gelatin and the rhythmic evolution of carbon monoxide during the dehydration of formic acid (A., 1919, ii, 504) has been applied to the rhythmic mercury-hydrogen peroxide catalysis, and verified experimentally. An equation is developed, by means of which the accumulation constants,  $H'$ , are shown to be constant throughout the reaction.

CHEMICAL ABSTRACTS.

**Structure of Matter and the Quantum Theory. F. H.**

LORING (*Chem. News*, 1920, 120, 181—184, 193—196, 205—207, 217—219).—Atomic weights are derived from that of hydrogen,  $H=1.008$ , by what is called an "electromagnetic multiplication table":

If	$1 \times 1.008 = 1.008$ ( $a$ ),
and	$4 \times 1.008 = 4.000$ ( $d$ ),
then	$2 \times 1.008 = 2.004$ ( $b$ ),
and	$3 \times 1.008 = 3.002$ ( $c$ ),

where  $a$ =hydrogen;  $d$ =helium;  $b$ =nitrogen sub-atom;  $c$ =fluorine sub-atom. Carbon and oxygen should then be:  $C=3He=12.000$ ;  $O=4He=16.000$ . Nitrogen and fluorine are:  $N=3He+b=14.004$ ;  $F=4He+c=19.002$ . The changes of mass in the table are assumed to have their origin in energy changes during the condensation of the constituents of the complex atoms. If helium atoms are assumed as units of atomic structure (4.000), and atomic outriders, or sub-atoms,  $a$ ,  $b$ ,  $c$ ,  $d$ , added, the results are said not to differ appreciably from the accepted atomic weights. The main results obtained in connexion with the quantum theory and positive rays are summarised. The author speculates on atomic structure, isotopes, and valency.

J. R. P.

**The Atomic Weight of Hydrogen and its Relation to Prout's Hypothesis.**

ALOIS BILECKI (*Zeitsch. anorg. Chem.*, 1920, 110, 335—338).—It has been shown in a previous paper (A., 1917, ii, 197) that the atomic weights of a number of elements are multiples of  $n=0.3076923$ , where  $n=16/52$ . It is now shown that  $n/40 = 0.007692307$ , is a number of fundamental importance. A critical examination of published determinations of the atomic weight of hydrogen ( $O=16$ ) establishes the value 1.0077 for this quantity. The fraction 0.0077, it is pointed out, is almost exactly equal to  $n/40$ .

E. H. R.

**The Atomic Weight of Phosphorus in Relation to that of Silver.**

ALOIS BILECKI (*Zeitsch. anorg. Chem.*, 1920, 110, 339—340).—The fundamental number  $n$  (preceding abstract) becomes  $n_1=0.307350427$  when  $Ag=107.88$  instead of 108. The atomic weight of phosphorus, determined through the halogens with respect to  $Ag=107.88$ , is practically identical with  $101n_1=31.04235$ .

E. H. R.

**The Relation of the Atomic Weight of Barium to that of Silver.** ALOIS BILECKI (*Zeitsch. anorg. Chem.*, 1920, **110**, 341—344).—The atomic weight of barium ( $A_g=107.88$ ),  $137.37$ , is practically identical with  $447n_1=137.38563$ , where  $n_1=0.307350427$ . When the atomic weight is found by analysis of the bromide, the value found is  $0.011\%$ , and by analysis of the chloride,  $0.0403\%$  low. E. H. R.

**Radioactive Disintegration of the Atomic Nucleus.** HANS TH. WOLFF (*Physikal. Zeitsch.*, 1920, **21**, 175—178).—A theoretical paper in which, accepting the hypothesis of Lindemann (A., 1915, ii, 720) that the instability of the atomic nucleus depends on a large number of particles which move independently inside the nucleus, and assuming that these particles follow Bohr's law in respect of the moment of impulse in their orbital motion, and that the velocity of the  $\alpha$ -particle is the same within the nucleus as it is outside, a formula is deduced, from the Geiger-Nuttall relationship between the disintegration constant and the range of the  $\alpha$ -particles and from the relationship between the velocity and range of the  $\alpha$ -particles, whereby the disintegration constant is expressed as a function of the rotation number of the particles which are expelled as  $\alpha$ -rays. A corresponding formula is developed from purely theoretical considerations, and an equation giving the conditions which must hold for both formulæ to be identical. The formulæ are applied to the case in which the motion, of the particles under consideration, undergoes no change during a single step in the disintegration of the atom. J. F. S.

**Arrangement of Electrons in the Elements of the Long Periods.** R. LADENBURG (*Naturwiss.*, 1919, **8**, 57; from *Chem. Zentr.*, 1920, i, 599—600).—In his previous communication (this vol., ii, 301), the author did not take into account certain definite results obtained by Baerwald in connexion with the irregularities in the atomic volume curve, since they were unknown to him at the time. H. W.

**The Binuclear Atomic Theory and the Disintegration of Nitrogen.** O. HINSBERG (*Chem. Zeit.*, 1920, **44**, 294).—The observation of Rutherford (A., 1919, ii, 260) that by bombardment with  $\alpha$ -particles from radium-*C* the nitrogen atom is disintegrated, with the production of rapidly moving hydrogen particles, is in agreement with the author's theory that the elements of the fifth to the eighth groups of the periodic system possess two valency centres (A., 1919, ii, 505). Rutherford considers that the hydrogen nucleus which is separated from the nitrogen atom by the  $\alpha$ -particle is situated relatively far from the principal nucleus of the nitrogen atom. In all probability, Rutherford's principal helium-containing nucleus in the nitrogen atom is identical with the author's postulated quadrivalent nucleus, whilst his hydrogen-containing nucleus corresponds with the author's univalent nucleus in the nitrogen atom. E. H. R.

**Absolute Saturation of the Attractive Forces Acting between Atoms and Molecules.** M. POLÁNYI (*Zeitsch. Elektrochem.*, 1920, **26**, 161—171).—A theoretical paper in which the absolute saturation of the attractive forces between atoms and molecules is considered. Absolute saturation is defined as follows: If an atom or molecule attracts a molecule  $AB$  from infinity with a force  $F_{AB}$ , and each of the atoms separately with forces  $F_A$  and  $F_B$ , respectively, then when  $F_{AB} < F_A + F_B$ , an absolute saturation of the forces  $F_A$  and  $F_B$  takes place in the formation of the molecule  $AB$ . A number of cases are cited to show that absolute saturation is of common occurrence, among which are included adsorption of gases. It is shown also that in a non-additive field of force, particularly in interatomic and intermolecular fields, which show absolute saturation, the heat of formation of the molecule changes with its position in the field, even when the field is homogeneous. Hence it follows that non-additive fields, which exhibit absolute saturation, can only be produced from hetero-polar systems. J. F. S.

**Barger's Microscopical Method of Determining Molecular Weights. I. The Principle of the Method with Reference to the Molecular and Ionic Attraction of Solute for Solvent.** KUMAO YAMAKAMI (*Biochem. J.*, 1920, **14**, 103—113).—It is proved that the force which effects the volume change in the drops is not simply the vapour pressure, but also the osmosis through the thin film of liquid between the drops. When the length of interval between the drops is 2—3 mm., as much as five-sixths or six-sevenths of the volume change is attributable to osmosis. It is therefore possible to measure molecular weights or the degree of association or dissociation by investigating the volume-change of drops which are brought in contact with drops of standard solutions of known molecular concentration. J. C. D.

**Valve for Glass Apparatus.** KURT BUNGE (*Chem. Zeit.*, 1920, **44**, 299).—The valve consists of a glass tube melted solid in one spot. On both sides of this are two small holes, not more than 10 mm. apart. A piece of coloured glass marks the position of the valve. A piece of rubber tubing is slipped over the valve, and the latter is operated by gentle pressure by the thumb and forefinger on the rubber. The valve may be used on burettes, or on pipettes to prevent liquid entering the mouth. J. R. P.

**Effective Connecting Bulb.** C. M. CLARK (*J. Ind. Eng. Chem.*, 1920, **12**, 366).—A bulb tube for preventing spray passing from a distillation flask into the receiver consists of a simple bulb on a tube, but the bulb has an internal baffle-plate in the form of a deep, inverted watch-glass; the latter is attached to the end of the upper tube (this end extends a short distance into the bulb), and the edge of the baffle-plate reaches to within 5 mm. of the side of the bulb. W. P. S.

**Manometer for Vacuum Distillation.** H. T. CLARKE (*J. Amer. Chem. Soc.*, 1920, **42**, 786).—A manometer is described, for use in vacuum distillation, which is designed to prevent liquid passing into the exhausted limb and also to prevent breakage if air should suddenly enter the distillation apparatus. The modification consists in the introduction of a hook-shaped trap half-way up the evacuated limb. The trap consists of a very fine capillary tube widened at one end and sealed to the walls of the manometer tube. This effectually prevents moisture getting into the exhausted space, and if the pressure suddenly drops it prevents the mercury rushing in and breaking the top of the manometer tube. J. F. S.

**A Device for Regulating the Temperature of Incubators either above or below Room Temperature.** JOHN H. NORTHRUP (*J. Gen. Physiol.*, 1920, **2**, 309—311).—The water flow through the jacket of a double-walled incubator is regulated by causing a relay to direct a stream of water either through the incubator or to waste as required by the temperature changes. This is brought about by means of a wire attached to the armature of the relay and attached at the other end to a glass pipette at the end of a vertical rubber tube. The current necessary to move this wire and pipette is so small that it is unnecessary to use a secondary circuit. The regulator may be either of the mercury-toluene or bimetallic type. J. C. D.

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### Inorganic Chemistry.

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**Generation of Hydrogen by the Reaction between Ferrosilicon and Sodium Hydroxide Solution.** E. R. WEAVER (*J. Ind. Eng. Chem.*, 1920, **12**, 232—240).—The preparation of hydrogen from ferrosilicon, sodium hydroxide, and water is most economically effected by dissolving sodium hydroxide in water so as to form a 20—30% solution, mixing a portion of this solution and ferrosilicon in the reaction chamber, and when the temperature has reached 0° adding ferrosilicon and the remainder of the sodium hydroxide solution at a uniform rate in order to keep the temperature constant. About equal weights of ferrosilicon and sodium hydroxide may be used. Towards the end of the operation, the reaction mixture is cooled by means of an internal spray of water.  
W. P. S.

**The Constitution of Hydrogen Peroxide.** ANTONIO RIUS y MIRÓ (*Helv. Chim. Acta*, 1920, **3**, 347—365).—The validity of Willstätter and Hauenstein's argument against the unsymmetrical formulæ for hydrogen peroxide (A., 1909, ii, 566), based on the reduction of benzoyl peroxide to benzoic acid as distinguished from

benzoic anhydride, is weakened by the fact that water formed in the reaction might hydrolyse any anhydride formed. The same result has now been obtained, however, by reduction in boiling benzene solution with yellow phosphorus. In addition, potassium orthophosphate is the sole product of the reduction of potassium perphosphate by potassium iodide in acetic acid solution, or by ferrous or cobalt hydroxides in alkaline solution. It is also shown that sulphuric acid cannot be oxidised to persulphuric acid by permanganic acid, plumbic salts, or nickel peroxide. The majority of oxidations due to hydrogen peroxide are really hydroxylations, but, although this is contrary to the asymmetrical formula, the case of potassium permanganate shows it does not necessarily lead to the symmetrical formula. This formula does not explain the reducing properties of hydrogen peroxide, which the author attributes to weakly-bound hydrogen atoms. By anodic oxidation of solutions of potassium hydroxide containing potassium fluoride, up to 5.35% of hydrogen peroxide, calculated on the energy expended, was obtained (compare Riesenfeld and Reinhold, A., 1909, ii, 879). The action of ozone on fuming sulphuric acid (Schmidlin and Massini, A., 1910, ii, 498) and of perchromic acid on hydrogen peroxide were also examined, evidence of interaction being obtained in the latter case (compare Riesenfeld, A., 1909, ii, 51). The author suggests the

formula  $\begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{O} \cdots \cdots \text{O} \\ \diagdown \quad \diagup \\ \text{H} \end{array}$  for hydrogen peroxide, and proposes that per-

oxides of the general type  $\text{RO}_2\text{R}$  be called anhydro-hydroperoxides, to distinguish them from Baeyer's hydroperoxides,  $\text{RO}_2\text{H}$ . As a test for hydroperoxides which can only be examined in acid solution, and to which Riesenfeld and Mair's test cannot therefore be applied (A., 1912, ii, 156), hydrogen peroxide itself is suggested. One molecule of oxygen is liberated, whilst the anhydroperoxides merely form an additive product.

J. K.

**Viscosity of Sulphur.** C. COLERIDGE FARR and D. B. MACLEOD (*Proc. Roy. Soc.*, 1920, [A], 97, 80—98).—The viscosity of molten sulphur has been determined at a series of temperatures by the method of rotating cylinders. It is shown that the viscosity of twice distilled, but not gas-free, sulphur has the value 0.1094 *C.G.S.* units at 123°, and from this temperature it falls to a minimum of 0.0709 *C.G.S.* units at 150° and then rises to 0.0759 at 159°, when the rise becomes more marked, but nothing of the nature of a strict transition point is observed. Exposure to air in the molten condition, especially below 160°, has a marked effect on the viscosity from 160° upwards. The effect is a slow one, the viscosity continuing to rise for as much as forty-eight hours on exposure to the air for that time. The maximum for purified gas-free sulphur is reached at 200°, when the value is 215 *C.G.S.* units; the maximum for purified but not gas-free sulphur, after a long exposure to air, is reached at 190°, and has a value about 800 *C.G.S.* units. Crystallisation has an apparent, but probably

secondary, effect on the viscosity as measured at any temperature. It apparently raises the viscosity of a low-valued sample of sulphur and lowers the viscosity of a high-valued sample. The effect of crystallisation seems to disappear when the viscosity of the sample is about 300 *C.G.S.* units at 171°. Sulphuric acid appears to be the impurity which, after exposure to the air, causes the extreme variations which are found in the values of the viscosity of air-exposed sulphur. Changes in the viscosity are accompanied by a corresponding change in the amount of insoluble sulphur present.

J. F. S.

**A New Hydrogen Sulphide Generator.** BERTRAM DILLON STEELE and HENRY GEORGE DENHAM (*T.*, 1920, **117**, 527—529).

**Solubility of Gases in Water. Sulphur Dioxide.** FREESE (*Chem. Zeit.*, 1920, **44**, 294).—Determinations of the solubility of sulphur dioxide in water between 0° and 40° at 760 mm. have been made, and the results are given in grams and in litres of gas dissolved per litre of water. At 0° the solubility is 228.29, at 10° 162.09, at 20° 112.90, at 25° 94.08, at 30° 78.67, and at 40° 54.11 grams per litre.

E. H. R.

**Catalytic Synthesis of Ammonia.** M. GUICHARD, VAVON, CORNEC, CANTRAGREL, STEVENSON, APARD, and BOURDIOL (*Bull. Soc. d'Encour.*, 1920, **132**, 71—102).—The authors have investigated the catalytic manufacture of ammonia, especially as regards the suitability of various catalysts. Addition of magnesia or alumina greatly increases the life of catalysts, such as iron, cobalt, nickel, tungsten, and molybdenum, and a combination of two of these metals ensures greater catalytic efficiency. Iron-molybdenum was proved to be the most resistant and to give the highest ammonia concentration—more than 4%. Iron alone gave less than 1%, molybdenum less than 1.5%, nickel 3%, and cobalt 3%. The best method of preparation is by precipitation of ferric nitrate with ammonium molybdate, followed by ignition, and subsequent reduction. With perfectly dry gases, uranium is a suitable catalyst, but its combinations with cobalt and molybdenum are inferior. Uranium-nickel gives poor results, and uranium-tungsten is practically inert. The authors have made a partial study of the whole cycle of operations, including the circulation of the gases, the recovery of heat, absorption of ammonia under pressure, and the most suitable arrangement of the furnace. [See, further, *J. Soc. Chem. Ind.*, 1920, 362A.]

W. J. W.

**Vapour Pressure of Ammonia.** C. S. CRAGOE, C. H. MEYERS, and C. S. TAYLOR (*J. Amer. Chem. Soc.*, 1920, **42**, 206—229).—The vapour pressure of ammonia has been determined over the temperature range -78° to +70° by the manometric method. Several forms of manometer are described in the paper. Seven different samples of ammonia were used in the experiments, and these contained less than 1 part per 100,000 parts of non-con-



densing gas and less than 0.01% by weight of other impurities. The phenomenon of hysteresis was observed near the boiling point of ammonia with a commercial specimen which contained a small amount of air; this indicates the absolute necessity of very complete removal of dissolved gases for any accurate measurements of vapour pressure by the static method. The normal boiling point of ammonia was determined by both the static and the dynamic method, and the mean of the two results found to be  $-33.35^{\circ}$ . Empirical equations are deduced which represent the vapour pressure over the measured range; the results of 122 measurements between  $-78^{\circ}$  and  $+25^{\circ}$  agree with the values calculated by means of these equations to within 1 millimetre, and the results of 28 measurements between  $+25^{\circ}$  and  $+70^{\circ}$ , made with a calibrated piston gauge, agree to within 3 millimetres. The vapour pressure of ammonia is expressed between  $-80^{\circ}$  and  $+70^{\circ}$  by either of the equations  $\log_{10} p = 30.256818 - 1914.9569/\theta - 8.4598324 \log_{10} \theta + 2.39309 \times 10^{-3} \theta + 2.955214 \times 10^{-8} \theta^2$  or  $\log_{10} p = 12.465400 - 1648.6068/\theta - 0.01638646\theta + 2.403276 \times 10^{-5} \theta^2 - 1.168708 \times 10^{-8} \theta^3$ , where  $p$  is expressed in millimetres of mercury and  $\theta$  in degrees absolute (abs. degrees  $=^{\circ}\text{C} + 273.1$ ). The slope of the vapour pressure-temperature curve is obtained by differentiation of either of the above equations.

J. F. S.

**Preparation of Mixtures of Nitrogen and Hydrogen by Decomposition of Ammonia.** R. O. E. DAVIS and L. B. OLMSTEAD (*J. Ind. Eng. Chem.*, 1920, **12**, 316—317).—The catalytic decomposition of ammonia by heat in the presence of iron, first investigated by Ramsay and Young (T., 1884, **45**, 88), and subsequently by Perman and Atkinson (*Proc. Roy. Soc.*, 1905, **74**, 110), has been studied under manufacturing conditions, an electrically heated iron autoclave packed with iron turnings being used for the purpose. At  $370^{\circ}$  73% of the ammonia was decomposed, at  $470^{\circ}$  84%, at  $540^{\circ}$  94%, at  $650^{\circ}$  99.6%, and at  $735^{\circ}$  99.7%. In practice, about 100 cu. ft. per hour of the mixture of hydrogen and nitrogen could be obtained at  $675^{\circ}$  with a loss of 0.3 to 0.4% of ammonia. The equilibrium of a system  $\text{H}_2\text{--N}_2\text{--NH}_3$  at that temperature corresponds with about 0.02% of ammonia. The average time of contact was about five seconds. When copper was used as the catalyst, a temperature about  $200^{\circ}$  higher and longer contact were required, which is in accordance with the facts observed by Beilby and Henderson (T., 1901, **79**, 1245). [See, further, *J. Soc. Chem. Ind.*, 1920, 362A.]

C. A. M.

**The Discoverer of Phosphorus.** LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1917, **5**, 238—243).—In chemical literature, the discoverer of cobalt is sometimes mistaken for the discoverer of phosphorus, or at least their names are spelt in the same manner (Brandt). The German alchemist Brand (born 1625) discovered phosphorus in the year 1669, 1674, or 1677, whilst the discovery of cobalt was made (1733 or 1735) by the Swedish chemist Brandt (1694—1798) (compare A., 1919, ii, 511).

W. R. S.

**Preparation of Arsenic Trichloride from White Arsenic and Carbonyl Chloride.** L. H. MILLIGAN, W. A. BAUDE, and H. G. BOYD (*J. Ind. Eng. Chem.*, 1920, **12**, 221—223).—When carbonyl chloride is passed over a mixture of arsenic trioxide (80%) and carbon (20%) heated at 200° to 260°, arsenic trichloride is formed, the yield being almost quantitative. The method has been used as a means of utilising the impure "tail gas" from carbonyl chloride manufacture. It is probable that the treatment of inorganic compounds with carbonyl chloride in the presence of carbon as a catalyst may be used as a general method of chlorination.  
W. P. S.

**Reversible Oxidation of Arsenious Acid.** C. MATIGNON and J. ALLAIN LECANU (*Compt. rend.*, 1920, **170**, 941—943).—When arsenious oxide is heated with oxygen at temperatures varying from 400° to 480° and pressures of 127—180 atmos., a certain amount of oxidation occurs, the extent of oxidation, other things being equal, increasing with the temperature. Similarly, a concentrated solution of arsenious oxide in aqueous sodium hydroxide at 80° under a pressure of oxygen equal to 50 atmos. is oxidised to the extent of 10.9% in five hours.  
W. G.

**The Disposition of the Atoms and the Optical Rotation of Quartz and Sodium Chlorate.** J. BECKENKAMP (*Zeitsch. anorg. Chem.*, 1920, **110**, 290—310).—The structures suggested by previous workers for quartz, for example, those of Söhnecke and Bragg, do not account for optical rotation in directions perpendicular to the principal axis. In the structure now proposed, the silicon atoms form a rhombohedral lattice instead of a three-point screw system, as in Bragg's structure. The spiral structure only appears after the introduction of the oxygen atoms, when the total structure is seen to be composed of nine three-sided, prismatic lattices. The disposition of the oxygen atoms is such that the orientation of the valency directions is the same in horizontal or vertical molecular layers, and the optical rotation perpendicular to the vertical axis is then accounted for. The different kinds of twin crystals of quartz, and the relation of quartz to tridymite,  $\beta$ -quartz, and cristoballite, are discussed. Sodium chlorate has a structure similar to that ascribed by Bragg to calcite, the calcium atoms being replaced by sodium and the carbon by chlorine.  
E. H. R.

**Luminous Carbon Flames Regarded as Turbid Media.** HERMANN SENFTLEBEN and ELISABETH BENEDICT (*Kolloid Zeitsch.*, 1920, **26**, 97—100).—When an intense beam of light from an arc is projected on to a Hefner candle flame, the beam is bent from its original path and polarised. The authors have measured the amount of deflexion, the polarisation, and the intensity of the deflected beam. It is shown that the intensity of the deflected light varies strongly with the direction, in the sense that with increasing angle between the incident beam and the direction of

measurement it increases, for example, a change in the angle from  $45^\circ$  to  $140^\circ$  changes the intensity 300%. The fraction of the light which is polarised reaches a very definite maximum when the angle of observation is  $90^\circ$  to the incident light. At this angle, the fraction is 86%. The intensity of the deflected beam increases with decreasing wave-length; thus there is an increase in intensity of 150% as the wave-length changes from  $0.700\ \mu$  to  $0.475\ \mu$ . The experiments show that the carbon flame behaves in a manner analogous to that of a turbid medium. J. F. S.

**Removal of Carbon Monoxide from Air.** ARTHUR B. LAMB, WILLIAM C. BRAY, and J. C. W. FRAZER (*J. Ind. Eng. Chem.*, 1920, **12**, 213—221).—Of various absorbents and catalytic oxidising substances examined, a mixture of  $\text{MnO}_2$ , 50%;  $\text{CuO}$ , 30%;  $\text{Co}_2\text{O}_3$ , 15%; and  $\text{Ag}_2\text{O}$ , 5%, gave the best results. The silver oxide was precipitated in the moist mixture of the other oxides, the mass then dried and ground to size. This mixture acts indefinitely at the ordinary temperature against any concentration of carbon monoxide in air, provided that the air is dry. When used in gas-mask canisters, the latter must be provided with a calcium chloride drying chamber at the inlet, and the "life" of the canister is then limited solely by that of the drier. W. P. S.

**Constitution of Carbon Sub-oxide.** H. STANLEY REDGROVE (*Chem. News*, 1920, **120**, 209—210).—By means of a method of calculation due to the author, the following theoretical numbers are found: for  $\text{O}:\text{C}:\text{C}:\text{C}:\text{O}$ , mol. heat of combustion, 243.6 Cal.; mol. heat of formation, 47.4 Cal.; for  $\text{C} \begin{array}{c} \diagup \text{C} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}:\text{O}$ , mol. heat of combustion, 286.1 Cal.; mol. heat of formation, 4.8 Cal. A determination of the thermochemical data would enable the constitution of the compound to be settled. J. R. P.

**Carbonyl Chloride. III. Action of Carbonyl Chloride on Industrial Iron Containers.** M. DELÉPINE and L. VILLE (*Bull. Soc. chim.*, 1920, [iv], **27**, 288—290).—When it contains a little free chlorine, carbonyl chloride slowly attacks iron, and the resulting ferric chloride colours the carbonyl chloride yellow. The oxychloride free from chlorine will dissolve rust or the sub-carbonate of iron, and it is probably from this source that the ferric chloride in commercial carbonyl chloride comes. W. G.

**Phase Diagram of Potassium and Sodium Chlorides and their Etched Figures.** G. TAMMANN (*Nachr. Ges. Wiss. Göttingen*, 1919, 422—427; from *Chem. Zentr.*, 1920, i, 604).—Potassium and sodium chlorides form a continuous series of mixed crystals between  $660^\circ$  and  $500^\circ$ . Since neither salt has a transition point, the phenomena observed when the mixed crystals are cooled must be attributed to separation of the components. With diminishing temperature, therefore, either the attractive forces within

the molecules of the respective chlorides must increase, or those between the unlike molecules must be greatly weakened. The results obtained by etching the individual crystals at the ordinary temperature indicate that the intra-molecular forces of the potassium chloride crystal differ from those of the sodium chloride crystal, or, more precisely, that certain lattice regions are more closely united in the former, whilst such differences are not observed in the latter. In the light of these observations, it is surprising that Röntgen analysis indicates the same lattice for each crystal. A possible explanation of the etched figures, based on atomic lattice structure, is discussed.

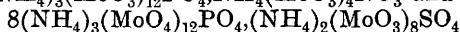
H. W.

**Preparation of Sodium Amalgam in Flakes.** ARTHUR D. HIRSCHFELDER and MERRILL C. HART (*J. Ind. Eng. Chem.*, 1920, **12**, 499).—To obtain sodium amalgam in readily pulverisable form the hot liquid amalgam is slowly poured into a vessel in which xylene or petroleum is mechanically agitated. The resulting flocculent deposit is dried on porous porcelain in a current of air.

C. A. M.

**The Variations in the Composition of Ammonium Phosphomolybdate.** S. POSTERNAK (*Compt. rend.*, 1920, **170**, 930—933).—Ammonium phosphomolybdate precipitated from phosphate solutions in the absence of ammonium salts always contains phosphorus and molybdic oxide in a constant ratio. It consists of a variable mixture of di- and tri-ammonium phosphomolybdates, varying according to the composition of the ammonium molybdate solution used.

In the presence of 5% or more of ammonium nitrate or sulphate the phosphomolybdate precipitate obtained is a complex mixture of the types  $16(\text{NH}_4)_3(\text{MoO}_3)_{12}\text{PO}_4 \cdot \text{NH}_4(\text{MoO}_3)_4\text{NO}_3$  and

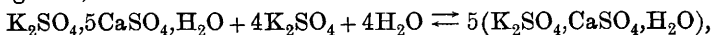


respectively. In all cases the molybdic acid behaves as though, in acid medium, it existed in the tetramolybdic state, and in this form combined with the hydroxyl groups of all the mineral acids present. This supports Kehrman's view as to the constitution of phosphomolybdic acid (compare A., 1887, 777).

W. G.

**Formation of the Double Salts of Calcium and Potassium Sulphates at 100°.** EVALD ANDERSON and R. J. NESTELL (*J. Ind. Eng. Chem.*, 1920, **12**, 243—246).—In determining the conditions of equilibrium for the formation of syngenite ( $\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and potassium pentacalcium sulphate at 100°, known weights of potassium sulphate and gypsum were shaken seven to twenty-three days with water in bottles immersed in boiling water, the resulting solutions rapidly filtered, and the potassium and calcium oxides and sulphuric anhydride estimated. Experiments were also made with previously prepared syngenite and potassium pentacalcium sulphate. The mean results showed that for the formation of the latter salt as in the equation  $5(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) + \text{K}_2\text{SO}_4 \rightleftharpoons \text{K}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot \text{H}_2\text{O} + 9\text{H}_2\text{O}$ , the equilibrium concentration for

potassium sulphate was 1.05 mols., and for the calcium sulphate 0.24 mol., per 1000 mols. of water. For the formation of the syngenite,



the equilibrium concentrations were 9.26 mols. of potassium sulphate and 0.142 mol. of calcium sulphate per 1000 mols. of water at 100°. These figures are considerably lower than those obtained by extrapolation from the results of D'Ans at 83°. Hence the value given by D'Ans for potassium sulphate is too high, or the equilibrium curve has a maximum between 83° and 100°.

C. A. M.

**Calcium Arsenates. I. Equilibrium in the System Arsenic Oxide, Calcium Oxide, Water at 35° (Acid Section).** C. M. SMITH (*J. Amer. Chem. Soc.*, 1920, 42, 259—265).—The equilibrium conditions between arsenic oxide, calcium oxide, and water have been determined at 35° for those mixtures in which the arsenic oxide is in excess and from which acid arsenates are likely to be produced. The results are recorded in a diagram to represent the phase rule relationships. Two compounds are found to be stable under the experimental conditions, dicalcium orthoarsenate monohydrate,  $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$ , which is identical with the mineral haidingerite, and monocalcium orthoarsenate,  $\text{CaH}_4(\text{AsO}_4)_2$ , which exist below and above, respectively, an acid concentration corresponding with 27.5% of arsenic oxide.

J. F. S.

**Atomic Weight of Radio-lead.** R. DE MONTESSUS DE BALLORE (*Rev. gen. Sci. pure et appl.*, 1919, 30, 673; from *Chem. Zentr.*, 1920, i, 558).—The figure 206 has been proposed for this atomic weight; a much more probable value is  $206.5 \pm 0.05$ .

H. W.

**Micrometallurgy.** ST. BOGDAN (*Bul. Soc. Chim. România*, 1919, 1, 60—72).—A micrographic study of the alloys of copper and silicon and iron and silicon. In all such alloys, when the percentage of silicon is very small, the result is a homogeneous solid solution. If the amount of silicon present exceeds 1%, crystalline compounds, embedded in the solid solution of the alloy, are always obtained, and are probably silicides. When the silicon content exceeds 4%, two crystalline silicides can be isolated, and also silicon in a crystalline and in an amorphous state. Prolonged heating of the alloys at high temperatures facilitates the separation of their components. As the proportion of silicon present increases further, the mass becomes more crystalline, the hardness increasing, the alloy becoming more friable.

W. G.

**Copper-Aluminium-Zinc Alloys of High Zinc Content.** E. H. SCHULZ and M. WAHLERT (*Metall. und Erz*, 1919, 16, 170—176, 195—201).—The thermal, structural, and mechanical properties of copper-aluminium-zinc alloys containing up to 10%

of copper and 10% of aluminium were investigated. Five sections of the three-dimensional equilibrium diagram are given, representing, respectively, alloys containing 2%, 4%, 6%, 8%, and 10% of copper with a varying aluminium content. A reproduction of the complete space diagram is also given, the principal features of which are two broad, curved surfaces intersecting in a eutectic line at  $375^{\circ}$ , running approximately parallel to the copper co-ordinate, and a second line, corresponding with 1.9% of copper, parallel to the aluminium co-ordinate, dividing the diagram into two unequal sections. The microscopic structure of the alloys confirms the conclusions drawn from their thermal study. Alloys containing less than 1.9% of copper and less than 0.75% of aluminium consist of homogeneous ternary mixed crystals. Those with more than 1.9% of copper and up to 0.8% of aluminium consist of a solid solution of  $\epsilon$ -crystals of the zinc-copper series with  $\alpha$ -aluminium crystals. The remainder of the alloys fall into five groups, according to the thermal equilibrium diagram, but only four of these can be distinguished by their structure.

The mechanical properties studied were the hardness, tensile strength, and crushing strength. No relation could be found between the tensile strength and the equilibrium diagram. The curves of equal hardness and of equal crushing strength, however, show an inflexion at a point which appears to correspond with the limit of solubility of zinc crystals in the alloys. E. H. R.

**Mechanism of the Formation and the Properties of Mercury Hydrosols prepared by Various Methods of Dispersion.** IVAR NORDLUND (*Kolloid Zeitsch.*, 1920, 26, 121—138).—Methods of preparing mercury sols by various methods are described. The methods are subdivided into three groups: (i) mechanical dispersion, (ii) thermal dispersion, and (iii) electrical dispersion. Mercury sols of small stability are produced when a fine stream of mercury is allowed to fall into a solution of potassium citrate ( $0.5-5 \times 10^{-3}N$ ) or a solution of gelatin (0.1%) with a velocity of 100 metres per second. In the latter case, a black coagulum is obtained, which consists of highly dispersed mercury and gelatin, and is readily peptised by warming with a trace of alkali to form a grey sol. Shaking mercury with conductivity water produces a very little of a rapidly sedimenting sol; the addition of potassium chloride, sodium chloride, potassium nitrate, potassium sulphate, copper sulphate, mercurous nitrate, and acetic acid to the water did not increase the sol formation. The presence of ammonia ( $1 \times 10^{-3}N$ ) in the water produced a sol which was not very stable, complete sedimentation occurring in two or three days. Ammonium chloride and sulphate solutions shaken with mercury produced sols which, in the case of ammonium chloride, were much more stable than in any of the previous cases. Shaking with a solution of potassium citrate ( $2-7 \times 10^{-3}N$ ) produced a very concentrated sol, which was coagulated by higher concentrations of citrate. This sol has a strong reddish-brown-grey colour, and is very stable. It may be kept for months without

coagulating. Shaking with solutions of carbamide (0.01%) and gelatin (0.0001—0.0025%) produced a dilute, grey sol. The formation of sols by the "spiriting" method is held to be due to a spontaneous atomising of the rushing mercury stream and to the atomising of the larger drops against the walls of the vessel. In the shaking experiments, the formation of sols is due to the disintegration of thin laminae of mercury; the bursting of mercury bubbles has little effect in sol formation. A deep brown, very concentrated sol was formed by distilling mercury from a porcelain retort through a red-hot silica tube, and thence through a fine jet into cold water. The mercury vapour entered the water with a velocity of 160 metres per second. The sol is not very stable, and in ten to fifteen minutes it had lost its brown colour, and in two or three days it had completely and irreversibly coagulated. Experiments, of the type often described, by electrical dispersion, both with direct and alternating current arcs, are also described. The partition of the radii of the particles has been worked out for the more stable of the sols described.

J. F. S.

**Compounds of Oxides.** (MLLE) S. VEIL (*Compt. rend.*, 1920, 170, 939—941).—Mixtures of ceric and chromic oxides in different molecular proportions were compressed and heated by methods similar to those used for alloys. The electrical conductivity at high temperatures and the coefficients of magnetisation at the ordinary temperature were then determined in each case. The curves showing the results indicate the existence of the compounds  $\text{CeO}_2, \text{Cr}_2\text{O}_3$ ,  $3\text{CeO}_2, 4\text{Cr}_2\text{O}_3$ ,  $\text{CeO}_2, 2\text{Cr}_2\text{O}_3$ , and  $\text{CeO}_2, 5\text{Cr}_2\text{O}_3$ , and the probable existence of the compounds  $5\text{CeO}_2, \text{Cr}_2\text{O}_3$ ,  $7\text{CeO}_2, 4\text{Cr}_2\text{O}_3$ , and  $\text{CeO}_2, 9\text{Cr}_2\text{O}_3$ .

W. G.

**The Reaction between Hydrochloric Acid and Potassium Permanganate.** F. P. VENABLE and D. H. JACKSON (*J. Amer. Chem. Soc.*, 1920, 42, 237—239).—It is shown that the reaction between potassium permanganate and hydrochloric acid and hydrobromic acid, respectively, takes place in two stages, which may, by regulating the quantity of acid employed, be separated. The reaction is represented: (i)  $2\text{KMnO}_4 + 8\text{HCl} = 2\text{KCl} + 2\text{MnO}_2 + 4\text{H}_2\text{O} + 3\text{Cl}_2$ ; (ii)  $\text{MnO}_2 + 4\text{HCl} = \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$ . It is also shown that hydrobromic acid reacts at a concentration 0.0015*N*, whilst with hydrochloric acid no reaction takes place until the concentration reaches 0.002*N*.

J. F. S.

**System Hydrated Ferric Oxide—Arsenious Acid.** WILHELM BILTZ (*Kolloid. Zeitsch.*, 1920, 26, 179—180).—A criticism of Oryng's paper (*A.*, 1918, ii, 317) on the adsorption compounds of ferric arsenite. Compare also Biltz and Utescher (*A.*, 1905, ii, 807).

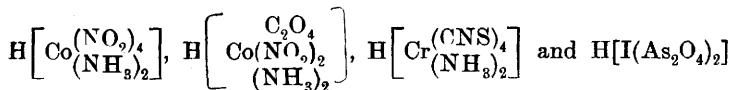
J. F. S.

**Influence of Superimposed Alternating Current on the Anodic Formation of Ferrates.** G. GRUBE and H. GMELIN (*Zeitsch. Elektrochem.*, 1920, 26, 153—161).—An investigation of

conditions under which sodium ferrate is formed by anodic oxidation in concentrated sodium hydroxide. It is shown that increasing temperature and alkali concentration favour large yields. With increasing current density the yield increases to a maximum, and then falls with any further increase in the current density. The current yield of sodium ferrate can be considerably increased by superimposing an alternating current over the direct current. The increase in the yield, for constant direct current, reaches a maximum for a definite alternating current density. Using as electrolyte 40% sodium hydroxide with an iron anode and a platinum cathode and electrolysing at 35° with a direct current of 3.33 amps./sq. dcm. and an alternating current of 5.0 amps./sq. dcm., an increase of 160% in the yield of sodium ferrate is obtained. In the preparation of concentrated solutions of ferrates the anode and cathode must be separated, and since ferrates lose oxygen at 50° and precipitate ferric hydroxide, this temperature must not be exceeded in the preparation, and the velocity of formation must be increased by imposing an alternating current on the direct current. In this way undecomposed saturated solutions and the crystalline salts may be obtained.

J. F. S.

**The Nature of Subsidiary Valencies. XXIV. Salts with High Ammonia Content.** FRITZ EPHRAIM and FRANZ MOSER (*Ber.*, 1920, **53**, [B], 548—563).—Recently, the addition of ammonia to salts containing a particularly large anion united to a small cation has been investigated, and it has been shown that ammines with unusually high ammonia content are thereby formed (*A.*, 1918, i, 389). In the previous communication, salts of organic acids were employed, but it is now shown that suitable inorganic complexes behave in a similar manner, and ammines of the acids



are now described. Addition of ammonia proceeds in many cases beyond the octammine stage, and, in extreme cases, leads to the liquefaction of the salts. The colour of the highly ammoniated compounds does not differ markedly from that of the hexammines, and the volume does not greatly increase when ammonia is added beyond the hexammine stage, whilst, also, reaction occurs without any great development of heat. The higher ammines do not exhibit a step-wise degradation to lower ammines with rise of temperature, but, generally speaking, gradually evolve ammonia in much the same manner as does a solid solution or adsorption compound.

The author extends his previous theory (*loc. cit.*) on the influence of the relative size of anion and cation on the properties of the salt. The presence of neutral portions (water, etc.) is supposed in a manner to fill the seams of the crystal caused by the unequal pairing of anion and cation, and thus to stabilise the whole structure. Addition of water as "packing material" increases the likeness of the



salt to water, and hence the solubility in water. The most sparingly soluble salts are therefore to be expected among such as contain most equally matched anion and cation; in general, the cation is spatially greater than the anion, the largest of the latter being represented by the alkali metals, particularly cesium; with voluminous anions (perchlorate, platinichloride, etc.) it is precisely this metal which forms the relatively least soluble salts, whilst the corresponding salts of other metals only crystallise after enlargement of the cation by the addition of neutral substances. Conversely, bulky basic radicles are best precipitated by acid radicles of compact structure ( $\text{ClO}_4$ ,  $\text{PtCl}_6$ , picric acid), quite apart from any question of basic character.

The following individual salts are described which, in general, are prepared by mixing suitable components in the presence of ammonia:

*Tetranitritodiamminocobalti-compounds*,  $[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]_2\text{M}$ .—Nickel: *hexammine* and *octammine*. Copper: *tetrammine* (+  $\text{H}_2\text{O}$ ), olive-green, microscopic prisms, and *octammine*. Zinc: *pentammine* and (?) *hexammine*.

*Oxalodinitritodiamminocobalti-compounds*.—Nickel: *octammine*, stable at the ordinary temperature; *decammine*, formed at  $-13^\circ$ , and, possibly, *dodecammine* at still lower temperature. Copper: *tetrammine*, red needles, which did not further absorb ammonia at  $-18^\circ$ . Zinc: *tetrammine*, *hexammine*, and *octammine*. Cadmium: *tetrammine*, pale red crystals which do not absorb ammonia.

*Tetrathiocyanatodiamminochromi-compounds*.—Nickel: *tetrammine*, which passes into the *nonammine* at the ordinary temperature and becomes completely liquefied when treated with ammonia at  $-20^\circ$ . Copper: (?) *tetrammine* and *octammine*. Cadmium: *decammine*, which becomes partly liquid when treated with excess of ammonia at  $-20^\circ$ . Zinc: *monammine*, *octammine*.

*Compounds derived from  $\text{H}[\text{I}(\text{As}_2\text{O}_3)]$*  (compare Weinland and Gruhl, A., 1919, ii, 411).—Zinc: *heptammine*, which passes through a series of solid solutions to the *hexammine* (at  $70^\circ$ ), which is converted to the *tetrammine* (at  $87^\circ$ ); the latter is stable up to  $200^\circ$ , but at  $210^\circ$  passes into the *diammine*. Nickel: one molecule of salt combines with the following numbers of molecules of ammonia: 16.1 at  $-20^\circ$ ; 14.2 at  $+18^\circ$ ; 10.3 at  $66^\circ$ ; 1.2 at  $77^\circ$ .

Attempts to obtain disulphitetetramminocobalti-, heptanitroso-sulphonicferri-, and dinitrosothiosulphatoferri-salts of the heavy metals were unsuccessful. Salts such as copper metachloroantimonate are decomposed by ammonia into their components, which then separately absorb the gas.

H. W.

**Reversible Reactions of Water on Tungsten and its Oxides.** GEORGES CHAUDRON (*Compt. rend.*, 1920, 170, 1056—1058).—At  $850^\circ$  the two reversible reactions may be expressed by  $\text{W} + 2\text{H}_2\text{O} \rightleftharpoons \text{WO}_2 + 2\text{H}_2 + \text{L}_{850}$  and  $2\text{WO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{W}_2\text{O}_5 + \text{H}_2 + \text{L}_{850}$ . The value of  $\text{L}_{850}$  for the first reaction is  $2 \times 4.4$  Cal., and for the second 4 Cal.

W. G.

**Solubility in the Solid State of Tin in Lead.** N. PARRAVANO and A. SCORTECCI (*Gazzetta*, 1920, **50**, i, 83—92).—In view of the discordance between the values given by different investigators for the solubility of tin in lead in the solid state (compare Rosenhain and Tucker, A., 1908, ii, 1038; Degens, A., 1909, ii, 888; Mazzotto, A., 1911 ii, 889; Parravano and Sirovich, A., 1912, ii, 846; Guertler, *Metallographie*, 736, and *Zeitsch. anorg. Chem.*, 1916, **98**, 97), the authors have measured the electrical conductivities of a series of nineteen tin-lead alloys at various temperatures lying between that of the air and that of the eutectic alloy.

The conductivity isotherms are found to consist of two branches, that in the neighbourhood of the lead axis indicating the existence of solid solutions. The limits of miscibility in the solid state of tin in lead, corresponding with the points of intersection of the two branches, show that the percentages of tin in the saturated solutions at different temperatures are as follows: 14.5 at 175°; 13.5 at 170°; 12.5 at 162°; 10 at 150°; 6.5 at 100°; 5.0 at 75°; 3.0 at 50°; and 1.5 at 25°. These values differ considerably from those given by Rosenhain and Tucker and from those assumed by Guertler, the first three of them being in moderately good agreement with Mazzotto's figures.

The curve along which tin separates from its solid solutions in lead at temperatures below the eutectic temperature is very regular, and confirms the conclusion that the recalescence observed with the solid alloys is due to a simple supersaturation phenomenon.

T. H. P.

**Colloidal Rhodium.** C. ZENGHELIS and B. PAPACONSTANTINOU (*Compt. rend.*, 1920, **170**, 1058—1061).—Colloidal rhodium may best be prepared by the following process. The metallic rhodium, after suitable purification, is converted into the double chloride,  $\text{Na}_3\text{Rh}_2\text{Cl}_{12}$ . This is dissolved in water, and to the slightly alkaline solution a solution of sodium protalbate is added and then a suitable reducing agent. Of the reducing agents tried, formaldehyde at 40° in a slightly alkaline solution is the most satisfactory, and under these conditions a clear, colloidal solution of rhodium is obtained. On purification by dialysis and subsequent evaporation to dryness in a vacuum, ebony-black plates are obtained which contain 33% of rhodium.

The colloidal solution of rhodium absorbs hydrogen to the extent of 2510—2960 times the volume of rhodium present. Similarly, the rhodium absorbs 346 times its volume of carbon monoxide at 12—14° and 1820 times its volume at 60°. The colloidal solution, slightly alkaline, causes a very slight combination of nitrogen and hydrogen to give ammonia, the reaction being considerably enhanced if the solution is made just acid with very dilute tartaric acid in the presence of potassium tartrate.

W. G.

## Mineralogical Chemistry.

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**Colouring Matters of Red and Blue Fluorite.** CECIL STEVENSON GARNETT (T., 1920, **117**, 620—622).

**Aphthitalite (= Glaserite) from Searles Lake, California.** W. F. FOSHAG (*Amer. J. Sci.*, 1920, [iv], **49**, 367—368).—Colourless, tabular, rhombohedral crystals were found embedded in powdery borax in a well boring at this locality. Material collected for analysis showed under the microscope some admixed halite. The following figures correspond with  $K_2SO_4$ , 72·37;  $Na_2SO_4$ , 18·38; NaCl, 7·87%, or  $K_2SO_4:Na_2SO_4$  about 4:1.

K.	Na.	SO <sub>4</sub> .	Cl.	H <sub>2</sub> O.	Total.
32·46	9·01	53·71	4·76	0·10	100·04
L. J. S.					

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### Analytical Chemistry.

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#### Substitutes for Platinum Wire for Flame and Bead Tests.

C. C. KIPLINGER (*J. Ind. Eng. Chem.*, 1920, **12**, 500).—Borax beads may be made by heating the "lead" from a blacklead pencil to redness, dipping it into borax, and again placing it in the flame, so that a drop of the melted substance is suspended from the end. In using a roll of filter paper instead of platinum wire for flame tests (Ehringhaus, this vol., ii, 263), a flame of longer duration is produced, by introducing the rolled slip into a glass tube, with constricted opening, containing the solution or the substance moistened with hydrochloric acid. About 3 cm. of the paper is allowed to project, and the tube is inclined so as to feed the wick thus formed.

C. A. M.

**Thioacetic Acid as a Reagent.** NAZARIO ALVAREZ (*Bol. minero soc. nac. min. Chile*, 1919, **31**, 181—191).—Finely powdered phosphorus pentasulphide (300 grams) and glacial acetic acid (300 grams) are mixed in a 2-litre flask containing glass beads (150 grams) to prevent ignition, and the mixture is carefully heated to a temperature not exceeding 100°; thioacetic acid begins to distil at 91°. Redistillation of the liquid serves to remove traces of arsenic and antimony. The ammonium salt is obtained by adding a slight excess of 10% ammonia to 10 c.c. of thioacetic acid. By diluting this solution to 30 c.c. a 33% solution of ammonium thioacetate is obtained, which, used in acid solution at 80—90°, has advantages (control of quantity, temperature, etc.) over hydrogen

sulphide for the precipitation of the bases of group II as sulphides; the filtrate, which contains ammonium chloride, is rendered available for the next group by boiling to remove hydrogen sulphide. The solution of ammonium thioacetate is not stable, and should be prepared when required for immediate use.

CHEMICAL ABSTRACTS.

**Device for Preventing Over-titration.** R. ORTHNER (*Chem. Zeit.*, 1920, **44**, 282—283).—A tube of about 5 mm. internal diameter, open at the top and constricted to a moderately fine jet at the lower end, is suspended vertically in the beaker containing the solution to be titrated; a short bent side-arm near the top of the tube is hooked over the edge of the beaker to keep the tube in position. The portion of the solution contained in this tube is not acted on by the reagent during the titration; the main portion of the solution is titrated until a very slight excess of reagent has been added; the tube is then raised so that its contents mix with the main portion of the solution, and the titration is completed.

W. P. S.

**Colorimetric Determination of Titration Curves.** LOUIS J. GILLESPIE (*J. Amer. Chem. Soc.*, 1920, **42**, 742—748).—A simple method is described for obtaining titration curves colorimetrically. The hydrogen ion exponents are determined without the use of buffer mixtures. Instead of a buffer mixture containing the indicator, a colour standard is used, consisting of a pair of test-tubes containing together 10 drops of indicator solution of suitable strength, the drop ratio in the two tubes being varied from 1:9 to 9:1. One tube of the pair contains dilute alkali and the other contains dilute acid. Reference to a table gives the hydrogen ion exponent corresponding with the drop ratio, or the exponent can be calculated from the relation  $P_H = k + \log (\text{drop ratio})$ , where the drop ratio is the ratio of the number of drops of the indicator solution in the alkali tube to that in the acid tube, and  $k$  is a constant depending on the indicator. It has the following values for the indicators named: tetrabromophenolsulphonephthalein, 4.1; methyl-red, 5.0; dibromo-*o*-cresolsulphonephthalein, 6.3; dibromothymolsulphonephthalein, 7.1; phenolsulphonephthalein, 7.7; *o*-cresolsulphonephthalein, 8.1; and thymolsulphonephthalein, 8.8.

J. F. S.

**Potassium Hydrogen Phthalate as a Standard in Volumetric Analysis.** W. S. HENDRIXSON (*J. Amer. Chem. Soc.*, 1920, **42**, 724—727. Compare A., 1915, ii, 797).—Potassium hydrogen phthalate is shown to be an excellent standard for volumetric work. It is best prepared from phthalic anhydride and potassium carbonate, and is obtained absolutely pure by three crystallisations. It contains no water of crystallisation, and is not hygroscopic, so that weighings may be made in open vessels. Its solubility has been determined in water, and the following values

obtained: 25°, 10.23%; 35°, 12.67%; and at the boiling point of the saturated solution, 36.12%.  
J. F. S.

**Automatic Methods of Gas Analysis depending on Thermal Conductivity.** E. R. WEAVER, P. E. PALMER, H. W. FRANTZ, P. G. LEDIG, and S. F. PICKERING (*J. Ind. Eng. Chem.*, 1920, **12**, 359—366).—An apparatus is described for the continuous analysis of gas mixtures by an electrical method depending on the thermal conductivity of the gas as compared with that of a standard gas or mixture. The apparatus is given in detail, and it may be adapted to record results automatically.  
W. P. S.

**New Forms of Combustion Apparatus for Use in Gas Analysis.** E. R. WEAVER and P. G. LEDIG (*J. Ind. Eng. Chem.*, 1920, **12**, 368—370).—A combustion pipette, of about 150 c.c. capacity, is provided with two short side-tubes, the outer ends of which are fitted with glass caps. These caps are cemented on and have short platinum leads passing through them, the inner ends of the leads connecting with a platinum spiral extending across the pipette from one side-tube to the other. A combustion capillary is also described; the igniting spiral of platinum wire extends vertically down a portion of the capillary between two short side-arms fitted with caps carrying the leads. This portion of the capillary is surrounded by a small water-jacket.  
W. P. S.

**Estimation of Chlorine with the Nephelometer.** ARTHUR B. LAMB, PAUL W. CARLETON, and W. B. MELDRUM (*J. Amer. Chem. Soc.*, 1920, **42**, 251—259).—The conditions to be observed in estimating traces of chlorine in alcohol and acetic acid solutions, by means of the nephelometer, have been investigated. It is shown that in a 50% alcohol water solution, heating silver chloride suspensions of widely differing concentrations at 40° for thirty minutes after precipitation produces a more intense and constant opalescence than can be attained at ordinary temperatures; further heating for thirty minutes at 40°, or keeping at the ordinary temperature for an hour, produces no perceptible change in this opalescence. Using this treatment, chlorides in such solutions may be estimated with an average deviation of 3—4% over concentrations ranging between 4 and  $300 \times 10^{-6}$  *N*. Opalescence in such solutions decays more rapidly in diffuse daylight than in the dark. The opalescence of the same quantity of silver chloride in water is about 15% greater than in 50% alcohol or in 50% acetic acid.  
J. F. S.

**Carbonyl Chloride. I. Detection and Estimation of Free Chlorine in Carbonyl Chloride.** MARCEL DELÉPINE (*Bull. Soc. chim.*, 1920, [iv], **27**, 283—286).—For the detection and estimation of free chlorine in carbonyl chloride by means of potassium iodide solution the concentration of the latter must not exceed 0.1%. After leading a known weight of the vapour of the carbonyl chloride into the potassium iodide solution, the free iodine is

titrated by means of standard thiosulphate. If the concentration of the potassium iodide solution exceeds 0.1% there is a risk of interaction between the iodide and the oxychloride with consequent liberation of iodine.

W. G.

**Carbonyl Chloride. II. Destruction of Carbonyl Chloride by Water; Estimation of Escaped Gases.** M. DELÉPINE, R. DOURIS, and L. VILLE (*Bull. Soc. chim.*, 1920, [iv], 27, 286—288).—Carbonyl chloride is only slowly decomposed by moisture in the air, but is rapidly decomposed by water, although in the latter case the presence of hydrochloric acid considerably retards the decomposition. For the estimation of traces of carbonyl chloride in the air, a known volume of the air is bubbled through 10 c.c. of a solution containing 1 c.c. of *N*-sodium hydroxide and 5 c.c. of 95% alcohol, the volume being made up with water. The liquid is then evaporated to 2 c.c. on a water-bath, 2 drops of acetic acid are added, and the whole is evaporated to dryness; the residue is taken up with 2 c.c. of water, again evaporated to dryness, and once more taken up with 2 c.c. of water and the chloride present titrated with *N*/40-silver nitrate. By this means it is possible to estimate the chlorine to 0.00005 gram.

W. G.

**Carbonyl Chloride. V. Estimation of Hydrogen Chloride in Carbonyl Chloride.** M. DELÉPINE, M. MONNOT, H. DUVAL, and J. LAFORE (*Bull. Soc. chim.*, 1920, [iv], 27, 292—295).—Five grams of finely powdered dry mercury cyanide are placed in a perfectly dry flask fitted with a ground-in stopper carrying two tubes. The carbonyl chloride is introduced into the flask in a sealed bulb, and the flask is exhausted. The bulb is then broken, and after twelve to fourteen hours the hydrogen cyanide formed by the action of any hydrogen chloride in the carbonyl chloride on the mercury cyanide is aspirated off and collected in 50 c.c. of 2*N*-sodium hydroxide, and is then estimated by Denigès's method.

W. G.

**Some Factors influencing the Estimation of Chlorides in Soil.** C. T. HIRST and J. E. GREAVES (*Soil Sci.*, 1920, 9, 41—51).—For the estimation of chlorides in soil the Volhard method gives more concordant and, as judged by the gravimetric method, more nearly exact results than the Mohr method. The following is the most satisfactory procedure to adopt. One hundred grams of finely powdered soil are shaken for five minutes with 500 c.c. of water and the solution is clarified either by the addition of 2 grams of alum or by filtration through a Pasteur-Chamberland filter. Twenty c.c. portions of the clear filtrate are transferred to stoppered bottles, and an excess of *N*/10-silver nitrate is added, followed by 10 c.c. of 95% alcohol. The mixture is shaken until the silver chloride is coagulated, after which 2 c.c. of a 4% ferric sulphate solution and 5 c.c. of dilute nitric acid are added, and the excess of silver nitrate is titrated with *N*/10-ammonium thiocyanate.

W. G.

**Estimation of Iodide and Bromide in Mineral Waters and Brines.** W. F. BAUGHMAN and W. W. SKINNER (*J. Ind. Eng. Chem.*, 1920, **12**, 358).—Iodides are estimated by the permanganate method (A., 1919, ii, 349). Another portion of the sample is distilled with ferric sulphate to remove iodine, the distillation then treated with a slight excess of ammonia, boiled, filtered, the filtrate evaporated to dryness, and the bromine estimated in this residue by the chromic acid method (this vol., ii, 48). W. P. S.

**Detection of Sulphuric Ions Masked in Complex Compounds.** P. JOB and G. URBAIN (*Compt. rend.*, 1920, **170**, 843—845).—The  $\text{SO}_4^{''}$  ion masked in complex cobalt compounds may be estimated by difference. The total  $\text{SO}_4^{''}$  is estimated in the ordinary way as barium sulphate, and the free  $\text{SO}_4^{''}$  is estimated by precipitation in the cold as benzidine sulphate. The difference between the two results gives the percentage of masked  $\text{SO}_4^{''}$  ions in the complex. W. G.

**Differentiation of Masked and Apparent Sulphuric Radicles in Complex Salts.** ANDRÉ KLING and DANIEL FLORENTIN (*Compt. rend.*, 1920, **170**, 993—995. Compare A., 1914, ii, 661).—A claim for priority over Job and Urbain (compare preceding abstract) for the use of benzidine hydrochloride in the estimation of free sulphate ions in complex cobalt salts. W. G.

**Solubility of Benzidine Sulphate in Water.** C. S. BISSON and A. W. CHRISTIE (*J. Ind. Eng. Chem.*, 1920, **12**, 485—486).—The solubility of benzidine sulphate in water at various temperatures was determined by evaporating a measured quantity of the solution, and also by titration with potassium permanganate solution in the presence of sulphuric acid. The solubility increased from 0.049 gram per litre at  $0^\circ$  to 0.290 (and 0.252) at  $80^\circ$ . The solution obtained at  $80^\circ$  was discoloured, even after twenty-four hours in a thermostat. This was probably due to partial oxidation of the benzidine, and accounts for the discrepancy between the results obtained by the two methods. The residue obtained at  $50^\circ$  (0.141 and 0.149 gram per litre) was only slightly discoloured, and probably gives the approximate solubility at that temperature. The results show that the smallest possible amount of cold water should be used for washing benzidine sulphate in the quantitative estimation of sulphate. C. A. M.

**Simplified Evaluation of Hyposulphite (Blankite; Redo).** G. BRUHNS (*Zeitsch. angew. Chem.*, 1920, **33**, 92).—The usual method of estimating hyposulphite by titrating a solution of the salt with potassium ferricyanide is subject to error on account of the rapidity with which the salt is oxidised in solution by atmospheric oxygen. The analysis can be carried out quickly and accurately in the following manner. In a porcelain dish are placed 20 c.c. of a standard potassium ferricyanide solution with a trace of ferrous sulphate sufficient to form a blue colloidal solution but not



a precipitate. A slight excess of the hyposulphite is weighed out in a scoop, and the salt is carefully dusted into the solution, with careful stirring, until the end-point, indicated by a change in colour from blue to bright reddish-yellow, is reached. The scoop is then weighed again to determine the weight of hyposulphite used. The accuracy of the method depends solely on the skill of the manipulator in dusting the powder into the solution. There is a small constant error due to the oxygen dissolved in the ferricyanide solution, but this is probably under 0.5%.  
E. H. R.

**Boric Acid Modification of the Kjeldahl Method for Crop and Soil Analysis.** F. M. SCALES and A. P. HARRISON (*J. Ind. Eng. Chem.*, 1920, **12**, 350—352).—The use of 4% boric acid solution as proposed by Winkler (A., 1913, ii, 527) for absorbing the ammonia in the distillation part of the Kjeldahl method is trustworthy. Bromophenol-blue is a suitable indicator for the subsequent titration.  
W. P. S.

**Method for Estimating Nitrogen in Sodium Nitrate by the Modified Devarda Method and the Use of the Davisson Scrubber Bulb.** C. A. BUTT (*J. Ind. Eng. Chem.*, 1920, **12**, 352, 354).—The reduction process described by E. R. Allen (A., 1915, ii, 575) is recommended, the scrubber bulb designed by Davisson (A., 1919, ii, 296) being used to prevent alkali spray passing into the receiver.  
W. P. S.

**Estimation of Nitrogen in Calcium Nitrate.** E. PLATOU (*Chim. et Ind.*, 1920, **3**, 310—312).—As manufactured in the Pyrenees by neutralising synthetic nitric acid with limestone, calcium nitrate contains on the average 76.15% of calcium nitrate and 21.45% of water, with small amounts (0.1—0.55%) of other salts of calcium, magnesium, iron, and aluminium. As the material is hygroscopic a fairly large sample (10 to 25 grams) should be dissolved, and portions of the solution taken. The most trustworthy method of estimating the nitrogen is to reduce it in alkaline solution by means of Devarda's alloy, and to distil the ammonia. [See also *J. Soc. Chem. Ind.*, 1920, 401A.]  
C. A. M.

**Estimation of Ammonia in Cultures in Presence of Urea.** PIERRE THOMAS (*Bull. Soc. chim. biol.*, 1919, **1**, 171—175).—To 50 or 100 c.c. of the liquid are added several drops of pure hydrochloric acid and 10% solution of lead acetate until no further precipitation occurs. A little finely powdered lead carbonate is then added, and the whole left for fifteen or eighteen hours. After filtration and washing with cold water, all the ammonia will be found in the filtrate, and the interference of phosphates will be prevented by the preliminary precipitation. The filtrate is introduced into a special form of apparatus, which is illustrated, and 5 grams of magnesium carbonate added. Ammonia is driven off by vacuum distillation below 40°, and is estimated by absorption in standard acid.  
J. C. D.

**Carbonyl Chloride. IV. Estimation of Carbonyl Chloride in Titanium Chloride.** M. DELÉPINE and J. LAFORE (*Bull. Soc. chim.*, 1920, [iv], 27, 290—292).—The method is based on the measurement of the carbon dioxide liberated when the carbonyl chloride is decomposed by water. A special apparatus is described, designed to overcome the difficulty due to the formation of plugs of oxide or oxychloride of titanium at the end of the inlet tube for the sample of titanium chloride. The carbon dioxide is aspirated off, collected in barium hydroxide, and estimated volumetrically.

W. G.

**Hydrolytic Decomposition of Alkali Aluminates and Methods of Determining the Concentration of Hydroxyl Ions in Concentrated Solutions of Alkali Hydroxides.**

ROBERT FRICKE (*Zeitsch. Elektrochem.*, 1920, 26, 129—151).—After a long account of the literature of the hydrolysis of alkali aluminates an account is given of an investigation of the so-called "crystalline" alumina obtained from solutions of the alkali aluminates and of the solutions in equilibrium with the precipitated alumina. Two methods are described whereby, from potential measurements of elements of the type  $\text{Hg}|\text{Hg}_2\text{Cl}_2||\text{sat. KCl}||\text{alkaline solution}|\text{PtH}$ , an approximate measure of the hydroxyl ion concentration of highly concentrated solutions of alkali hydroxide may be obtained. By this means it is shown that considerable difference occurs between the hydroxyl-ion concentration of sodium and potassium hydroxides in concentrated solutions. By means of titration experiments it is shown that the hydrolysis of alkali aluminates is a time reaction. The so-called crystalline alumina is not crystalline and possesses properties which vary with the age of the preparation. The ageing of alumina is proportional to the hydroxyl-ion concentration of the alkali solution in equilibrium with it. Measurements on the viscosity of solutions of alkali aluminates indicate that the sodium hydroxide molecule (or the sodium ion) is probably more strongly hydrated than the potassium hydroxide molecule (or the potassium ion). Freezing-point measurements and potential measurements show that aged solutions of aluminates contain considerable quantities of colloidal alumina.

J. F. S.

**Potassium Chlorate as a Standardising Substance for Solutions of Alkali.**

H. B. VAN VALKENBURGH (*J. Amer. Chem. Soc.*, 1920, 42, 757—760).—Potassium chlorate may be used as a standard in titrating alkali by the following method. The chlorate is dried at 240° for four to six hours, the solution is boiled in an Erlenmeyer flask, sulphur dioxide passed in for thirty minutes, and the boiling continued for a further ten minutes to remove all excess of sulphur dioxide. Phenolphthalein is then added, and the solution titrated either hot or cold with alkali. The calculation of the strength of the alkali is based on the equation  $\text{KClO}_3 + 3\text{SO}_2 + 3\text{H}_2\text{O} = 3\text{H}_2\text{SO}_4 + \text{KCl}$ . The results of titrations by this method agree with those obtained by titrating the alkali with standard acid.

J. F. S.

**Estimation of Potassium as Perchlorate. II.** GREGORY P. BAXTER and MATSUSUKE KOBAYASHI (*J. Amer. Chem. Soc.*, 1920, **42**, 735—742. Compare A., 1917, ii, 270).—The method of estimating potassium by the perchlorate method has, as a result of the publication of Gooch and Blake (A., 1918, ii, 20), been further investigated. The authors maintain the efficiency of the method previously published, with the modification that the initial extraction of the sodium perchlorate should be carried out with alcohol containing perchloric acid, but not potassium perchlorate, instead of with a saturated solution of the latter salt. When the quantity of sodium is small, the use of a saturated solution of potassium perchlorate for the initial washing is safe, but when the quantity of sodium is large, the potassium salt is best washed once or twice with alcohol containing perchloric acid before the use of the saturated solution of the precipitate is commenced. The chief points to be observed in the estimation are: (i) the use of absolute alcohol; (ii) a low temperature ( $0^{\circ}$  if possible); (iii) filtration in a platinum-sponge crucible; (iv) at least one solution of the precipitate in water and re-evaporation to dryness in the course of the washing; (v) the use of alcohol containing perchloric acid and saturated with potassium perchlorate at the temperature of washing, for washing the precipitate after the sodium salt has been removed by washing with alcohol containing perchloric acid. Using this method, the error is never more than a few tenths of a milligram. J. F. S.

**Iodic Acid a Microchemical Reagent for Soluble and Insoluble Compounds of Calcium, Strontium, or Barium.** G. DENIGÈS (*Compt. rend.*, 1920, **170**, 996—998).—Iodic acid, in 10% aqueous solution, gives almost immediately finely crystalline, characteristic precipitates of calcium, strontium, or barium iodate with salts of these metals. This serves as a basis for the microchemical detection of these metals. An insoluble salt is finely powdered and suspended in a drop of water on a microscope slide, and a drop of the iodic acid solution is added, the formation of the crystalline precipitate being observed under the microscope. A soluble salt is dissolved in water, one drop of the solution being used. If barium is present as the sulphate, this salt is best reduced by heating it on a platinum wire in a reducing flame, the test being applied to the resulting sulphide. Calcium iodate or periodate should be first ignited to the iodide before applying the test. W. G.

**The Spectrographic Detection of Metals and Specially of Zinc in the Animal Organism.** A. DE GRAMONT (*Compt. rend.*, 1920, **170**, 1037—1039).—Using the method of spectral analysis previously employed for the detection of titanium (compare A., 1918, ii, 49), zinc may readily be detected in the ash from cobra venom by its rays  $\lambda=4811$  and  $4722$  and the ultra-violet ray  $\lambda=3345$ . The method is also suitable for the detection of traces of iron. W. G.

**Rapid Estimation of Copper in Copper-Aluminium Alloys.** PIERRE HULOT (*Ann. Chim. anal.*, 1920, [ii], 2, 103).—A portion of the finely divided alloy is treated with 20% potassium hydroxide solution, which dissolves the aluminium. The insoluble residue of copper is then collected, washed, and weighed, or dissolved in nitric acid, converted into sulphate, and estimated electrolytically.

W. P. S.

**Detection of Manganese and Zinc in the Presence of Phosphates or Oxalates.** E. SCHMIDT (*Ber. deut. Pharm. Ges.*, 1920, 30, 217—218). Manganese and zinc are precipitated together by means of ammonium sulphide, and are then separated by a method based on the different solubilities of their respective hydroxides,  $Mn(OH)_2$  and  $Zn(OH)_2$ , in a solution of ammonia and ammonium chloride. Wester's statement (this vol., ii, 334) that in the presence of phosphoric or oxalic acid the metals are precipitated as phosphates or oxalates is incorrect, since the precipitates consist of sulphides even under these conditions. This is shown by the fact that on treating a solution of manganese sulphate containing ammonium chloride with ammoniacal ammonium sodium phosphate solution in excess, and then saturating the liquid with hydrogen sulphide, the precipitated manganese phosphate is converted into manganese sulphide. An addition of ammonium sulphide does not effect this conversion under these conditions.

C. A. M.

**Estimation of Iron in Iron Ores by means of Permanganate.** R. SCHWARZ (*Chem. Zeit.*, 1920, 44, 310—311).—In reply to the criticisms of Brandt (this vol., ii, 269) on the method of Schwarz and Rolfes (*A.*, 1919, ii, 170), experiments are described which show that colloidal silicic acid solutions have no disturbing influence on the results of the titration of iron in sulphuric acid solution. On the contrary, the sol in association with the manganous salt has a favourable influence on the titration of iron in hydrochloric acid solution. There is no evidence of the alleged formation of an intermediate persilicic acid.

C. A. M.

**Method for the Analysis of an Iron Ore.** ERNEST LITTLE and WILLARD L. HULT (*J. Ind. Eng. Chem.*, 1920, 12, 269—273).—The ore is dissolved in hydrochloric acid, the ferric salts are reduced, and the solution is diluted and treated with an excess of standardised potassium dichromate solution. Five grams of ammonium fluoride and 5 grams of potassium iodide are then added, and the iodine liberated by the excess of dichromate is titrated with thiosulphate solution. The ammonium fluoride prevents the action of the ferric salts on the iodide. The preliminary reduction of the ferric salts may be made with stannous chloride solution (avoiding an excess), mercuric chloride being added afterwards, but the use of the Jones' reductor is recommended.

W. P. S.

**Use of Cupferron in Quantitative Analysis.** G. E. F. LUNDELL and H. B. KNOWLES (*J. Ind. Eng. Chem.*, 1920, **12**, 344—350).—Cupferron (the ammonium salt of nitrosophenyl-hydroxylamine) has been used for the separation of iron from manganese, and iron and titanium from aluminium and manganese; its use has also been found trustworthy for the estimation of iron, copper, titanium, zirconium, thorium, and vanadium. In most cases, however, the "cupferron" method does not offer any advantages over ordinary established methods. The following substances interfere with the separations: silver, mercury, tin, lead, bismuth, cerium, tungsten, uranium, silica, and excessive amounts of phosphorus, alkalis, and alkaline earths. W. P. S.

**Influence of Atmospheric Oxygen on the Iodometric Estimation of Chromium.** OTTO MEINDL (*Zeitsch. anal. Chem.*, 1919, **58**, 529—548).—The iodometric estimation of chromium is affected by atmospheric oxygen, since the latter enters into the reaction between the chromic acid and hydriodic acid. The results obtained are too high, the error increasing with the time of contact. W. P. S.

**A Test for Molybdenite.** F. C. FUCHS (*Informaciones y mem. soc. ing. Peru*, 1918, **20**, 423).—The mineral to be tested is dissolved in fused potassium hydroxide. If molybdenum sulphide is present, it dissolves with an intense red colour. If the fused mass is cooled and dissolved in water, the colour changes to blue, green, yellow, etc., corresponding with the various states of combination of molybdenum. The reaction is explicable on the theory that molybdenum sulphide gives up one of its sulphur atoms to the fused potassium hydroxide, forming a red, double sulphide.

CHEMICAL ABSTRACTS.

**Estimation of Tungsten.** R. F. HEATH (*Chem. Trade J.*, 1920, **66**, 629).—The sample is fused with sodium peroxide, and the filtered extract of the mass treated with 6—7 c.c. of a solution prepared by dissolving 10.3 grams of stannous and 2.1 grams of stannic chlorides in 100 c.c. of dilute acetic and 40 c.c. of syrupy phosphoric acids. Three to four c.c. of sulphuric acid are added, and, after allowing the blue colour to develop for several minutes, it is compared with that produced by the reagent in solutions of known tungsten content. [See also *J. Soc. Chem. Ind.*, 1920, June.] A. R. P.

**Analysis of Tungsten.** JOSEPH ERLICH (*Ann. Chim. anal.*, 1920, [ii], **2**, 102—103).—The tungsten is heated with hydrochloric acid and ferric chloride, and the insoluble portion is collected, washed with ammonium nitrate solution, ignited, and weighed. The ignited residue is then fused with sodium hydrogen sulphate, dissolved in ammonia, and the solution treated with ammonium carbonate; the tungstic oxide remains in solution, and

the impurities, which are precipitated, are collected, ignited, weighed, and their weight deducted from the weight first obtained. The difference between the two weights gives the quantity of tungstic oxide present. Two fusions with sodium hydrogen sulphate may be necessary in order to separate all the impurities.

W. P. S.

### Estimation of Tungstic Acid in Tungsten Concentrates.

HÉRCULES CORTI (*Anal. Soc. Quim. Argentina*, 1917, 5, 308—326).—A detailed description is given of the estimation of tungstic acid in wolfram or scheelite concentrates by decomposing the finely powdered ore with hydrochloric acid, evaporating to dryness to render silica insoluble, dissolving the tungstic acid in the washed residue with ammonia, evaporating the filtrate, and igniting the residual  $\text{WO}_3$ . [See *J. Soc. Chem. Ind.*, 1920, June.]

W. R. S.

### The Salts of Nitrosophenylhydroxylamine (Cupferron) ; Uranous Salt. V. AUGER (*Compt. rend.*, 1920, 170, 995—996).—

In neutral solution, cupferron gives precipitates with all the metallic salts except those of the alkali metals, the precipitates obtained being divisible into simple salts, insoluble in chloroform and decomposed by dilute acids, and complex salts, soluble in chloroform and more or less resistant to concentrated acids.

Uranyl salts do not give precipitates with cupferron, but if they are first reduced by zinc to uranous salt, then the whole of the uranium is precipitated in acid solution by cupferron. The uranous salt obtained is soluble in chloroform, from which it crystallises in brown prisms,  $(\text{C}_6\text{H}_5\text{O}_2\text{N})_4\text{U}$ . Thus, by this means, vanadium and uranium may be separated by successive precipitation.

W. G.

### The Estimation of Uranium. R. SCHWARZ (*Helv. Chim. Acta*, 1920, 3, 330—346).—

Of the various precipitants recommended for uranium, mercuric oxide is untrustworthy, hydrogen peroxide is quite unsatisfactory, ethylenediamine has no advantages over ammonia, and hydrofluoric and oxalic acids are inconvenient. The simplest and most trustworthy agents are ammonium sulphide and ammonia. Precipitation with the former is best carried out at  $80^\circ$  in presence of ammonium chloride; some ammonium uranate is always formed, and, further, complete separation from the alkali metals is only attained by repeating the precipitation. Precipitation with ammonia should be performed at  $100^\circ$  in presence of ammonium chloride, and preferably not in glass vessels, owing to the tendency of ammonium uranate to carry silica with it. Ignition of the precipitate from either process to uranosouranic oxide (Zimmermann, A., 1886, 598) is best carried out in porcelain crucibles with access of air, since platinum permits diffusion of gases from the flame, and consequent reduction. Its reduction by means of hydrogen to uranous oxide is not quanti-

tative (Kern, A., 1902, ii, 51), owing to the formation of nitride. The separation of uranium from the alkali metals in the form of uranyl phosphate (Kern) was found to be almost impossible owing to the fineness of the precipitate obtained. Of volumetric processes, that involving the solution of uranosouranic oxide in sulphuric acid (Boller, *Diss.*, Zurich, 1915) was simplified and gave good results; this was not the case, however, if complete reduction to urano-salts were first attempted (compare Pulmann, A., 1903, ii, 761). The estimation of uranium in presence of aluminium is most conveniently performed titrimetrically. The precipitation of aluminium by means of ammonium carbonate in presence of ammonium salts is incomplete, and some uranium is also carried down; a complicated procedure, which, however, gives good results, is necessary to effect complete separation. Contrary to Kern's view, Pisani's process (1861) for the separation of iron from uranium by ammonium carbonate and ammonium sulphide is quite effective. Ditte's process (this Journ., 1877, ii, 926) for the separation from chromium salts is unsatisfactory (compare Formánek, A., 1890, 852), and they must first be oxidised to chromate, most suitably by alkaline hypobromite, although Jannasch's ammonium persulphate method gives exact results. Sodium uranate, when precipitated in presence of chromate (Gibbs, this Journ., 1874, 93), always contains uranyl alkali chromates, and the precipitation must therefore be repeated; it is also advisable to redissolve the uranosouranic oxide finally obtained in nitric acid to separate it from silica.

A redetermination of the dissociation tension of uranosouranic oxide gave results differing from those of Colani (A., 1907, ii, 878), and, taken in conjunction with the heat of formation of uranosouranic oxide from uranous oxide (Mixer, A., 1912, ii, 899), indicate the existence of an intermediate oxide. Further, by igniting the higher oxide in a stream of carbon dioxide in an electric furnace at  $1122^{\circ}$ , a black residue was obtained corresponding approximately in composition with the formula  $U_2O_5$ ; traces of nitride were produced when nitrogen was employed. The contrary results of Zimmermann (*loc. cit.*) were vitiated by his use of a platinum crucible over a gas flame, which permitted reduction. For the same reason, the ignition of chromic oxide is best carried out in a platinum crucible, since this avoids the formation of chromichromate otherwise observed (Rothang, A., 1914, ii, 73). J. K.

**Estimation of Nitroform by Potassium Permanganate.** PHYLLIS VIOLET McKIE (T., 1920, 117, 646—648).

**Reactions of Chloropicrin.** GUILLEMARD and LABAT (*Bull. Soc. pharm., Bordeaux*, 1919; from *Ann. Chim. anal.*, 1920, [ii], 2, 120—121).—The odour of chloropicrin is destroyed by alkali polysulphide solution. When a drop of chloropicrin is boiled with alcoholic potassium hydroxide solution and a small quantity of thymol, a yellow coloration is obtained; if the thymol is replaced by resorcinol, the coloration is red. The addition of sulphuric acid

to the alkaline thymol mixture produces a reddish-violet coloration, and the whole mixture, on dilution with acetic acid, exhibits an absorption band in the green portion of the spectrum. Chloroform yields slightly different colorations under the above conditions, but a mixture of chloroform and a trace of sodium nitrite yields the same reactions as does chloropierin. Both chloroform and chloropierin yield a carbylamine. When chloropierin is boiled with potassium hydroxide solution, the mixture, after cooling, yields reactions characteristic of nitrous acid. W. P. S.

**Estimation of Methyl Alcohol.** S. B. SCHRYVER and CYRIL CHRISTIAN WOOD (*Analyst*, 1920, **45**, 164—170).—A method for the estimation of methyl alcohol in aqueous solution is described, the essential principle of the method being the determination of the concentration of ammonium persulphate necessary to destroy completely the formaldehyde formed in the initial stages of the oxidation process under certain specified conditions of experiment. The formaldehyde is detected by the phenylhydrazine hydrochloride and potassium ferricyanide test described previously by one of the authors (Schryver, A., 1910, ii, 335). By slight modification, the method may be used for the estimation of methyl alcohol in acetone. To estimate methyl alcohol in ethyl alcohol, the mixture of alcohols is oxidised partly by a relatively small amount of persulphate (the alcohols being in excess), and the formaldehyde formed is estimated colorimetrically. [See, further, *J. Soc. Chem. Ind.*, 1920, June.] W. P. S.

**Use of Diastatic Reagents in Analytical Investigations. Differentiation between Guaiacol and Creosote.** LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1917, **5**, 305—307).—Creosote is known to have been used as a substitute for guaiacol in medicinal preparations. They may be differentiated by dissolving the residue from the chloroform extract of the sample in alcohol and adding a direct oxydase. In presence of guaiacol, a yellow coloration is obtained at once, which gradually turns orange. Creosote under the same conditions gives no colour; after more than half an hour, a slight violet tint develops. If a few drops of hydrogen peroxide are also added to the test, guaiacol gives a more intense colour, whilst creosote furnishes a strong, reddish-violet coloration; indirect oxydases may be used when hydrogen peroxide is added. It is recommended to carry out the reactions in dilute solution. W. R. S.

**The Systematic Detection of Acetates.** L. J. CURTMAN, D. A. BROGGI, and V. FOURMAN (*Chem. News*, 1920, **120**, 230).—To detect acetates in mixtures, the following procedure is recommended. The solution is acidified with 10% nitric acid and 5 c.c. in excess added, followed by *N*/4-silver nitrate until no further precipitate is formed. After filtering, the clear liquid is made just alkaline with sodium hydroxide, and 10 c.c. each of 2*N*-barium chloride



and 2*N*-calcium chloride solutions added. The precipitate is filtered off, and the filtrate evaporated to 5 c.c. after addition of 10 c.c. of 3% hydrogen peroxide. The crystals are filtered off, and the filtrate made just neutral to phenolphthalein with hydrochloric acid. One c.c. of *N*/2-ferric chloride solution is added, and the colour compared against that of 1 c.c. of the reagent in 5 c.c. of water. Two mg. of acetic acid give a pale reddish-yellow colour. The odour of acetic acid is perceptible if 1 c.c. of a solution containing at least 2 mg. of the acid is boiled with 2 c.c. of 1:1 sulphuric acid, but nitrates seriously interfere with the test.

A. R. P.

**Estimation of the Total Non-amino-organic Acids in Urine.** A. DESGREZ and M. POLONOWSKI (*Compt. rend.*, 1920, 170, 1008—1010).—One hundred c.c. of the urine are made alkaline with sodium carbonate and evaporated to dryness on a water-bath. The residue is mixed with pure sand moistened with a slight excess of phosphoric acid, and the whole is extracted with ether containing 1% of alcohol in a Louise apparatus for ten hours. To the ethereal extract a known volume of *N*-sodium hydroxide is added, and the excess is titrated with *N*-sulphuric acid.

To obtain some idea of the molecular weight of the non-amino-acids and to correct for any hydrochloric acid present, the ethereal extract is shaken several times with a solution of barium hydroxide. The insoluble barium salts are collected, washed, dried at 110°, weighed, ignited to barium carbonate, and weighed again. These two weighings give a means of calculating the average molecular weights of the barium salts insoluble in water. The filtrate from the above precipitate is freed from excess of barium by carbon dioxide, and the solution is filtered, evaporated to dryness, and the residue weighed. By calcination, the organic barium salts are converted into carbonates, and the residue is again weighed. The carbonate is converted into chloride, and the total chloride is dried and weighed. The three weighings allow of a calculation of the amount of chloride mixed with the organic salts, the total weight of the latter, and their average molecular weight.

W. G.

**A New Reaction of Acraldehyde.** LUCAS TSALAPATANIS (*Anal. Soc. Quim. Argentina*, 1917, 5, 244—245).—The liquid to be tested is heated with 1—2 c.c. of an aqueous solution of resorcinol and a few drops of 10% sodium hydroxide solution. After two minutes, a bluish-green coloration appears in dilute, and a red one in concentrated, solutions. The reaction is extremely sensitive. The colour, which is very stable, is destroyed by acids, but restored by sodium hydroxide.

W. R. S.

**Microchemical Method for the Estimation of Sugar in Body Fluids.** R. GOIFFON and F. NEPVEUX (*Compt. rend. Soc. Biol.*, 1920, 83, 121; from *J. Pharm. Chim.*, 1920, [vii], 21, 357—359).—A portion of the fluid, after suitable clarification, is boiled with Fehling's solution, the cuprous oxide is collected,

washed, dissolved in a minimum quantity of hydrochloric acid, a few drops of potassium ferrocyanide solution and three drops of saturated tartaric acid solution are added, and the coloration obtained is compared with those shown by standards prepared under similar conditions from known amounts of sugar.

W. P. S.

**The Iodometric Estimation of Sugars.** HILDA MARY JUDD (*Biochem. J.*, 1920, **14**, 255—261).—Estimation of lævulose in fruit juices by the polarimetric method is untrustworthy. Various iodometric methods for the estimation of aldoses in the presence of ketoses have been tested, and none of them was found to give quantitative results. This is ascribed to the action of the dilute alkalis on the sugars. In using either the method of Colin and Lievin (*A.*, 1918, ii, 461), or that of Willstätter and Schudel (*A.*, 1918, ii, 337), a definite and constant weight of iodine always reacts with a given weight of dextrose. This weight of iodine is not affected by the changes in the amount of alkali present, or by the presence of other sugars. This is also true of lævulose. It is therefore possible to calculate the amount of dextrose and lævulose in a solution from the copper-reducing power and the iodine figure. Each sugar has its own characteristic iodine value. Rhamnose behaves very abnormally. Sucrose is not oxidised, whilst lactose and maltose are both oxidised, the former requiring twice as much iodine as the latter.

J. C. D.

**Estimation of Sugars by Inversion.** E. HILDT (*Ann. Chim. anal.*, 1920, [ii], **2**, 103—106).—A discussion regarding methods for the inversion of sugars. Chemical catalysts possess advantages over enzymes, since they have a definite action under given conditions. Certain aromatic sulphonic acids (benzenesulphonic acid, etc.) are particularly useful for this purpose, especially in the estimation of sugars in sweetened condensed milk.

W. P. S.

**A Cryoscopic Method for the Estimation of Sucrose.** HENRY H. DIXON and T. G. MASON (*Sci. Proc. Roy. Dubl. Soc.*, 1920, **16**, 1—8).—The method consists in determining the freezing point of the solution before and after the inversion of the sucrose by invertase. The freezing point is determined by the thermoelectric method described by Dixon (compare *A.*, 1911, ii, 853). In the case of plant sap, the tissues are frozen and the sap pressed out. The sap is boiled and filtered, and weighed quantities are cooled in test-tubes to  $-2^{\circ}$ . The requisite amount (0.33 gram) of invertase is added and the freezing point determined. The mixture is then incubated at  $28^{\circ}$  for twenty-four hours and the freezing point again determined. The increase in the depression of the freezing point is a measure of the sucrose originally present. A preliminary removal of gums, etc., from the sap is not necessary. Using 2.5 c.c. of sap the probable error is 0.0016 gram of sucrose.

W. G.

**Estimation of Amino-acids by means of the Hydrogen Electrode.** E. L. TAGUE (*J. Amer. Chem. Soc.*, 1920, **42**, 174—184).—Neutralisation curves have been obtained for the amino-acids, lysine dihydrochloride, glutamic acid, tyrosine, phenyl-alanine and glycine. The method consists in adding standard alkali hydroxide solution to a definite volume of an aqueous solution of the acid and measuring the hydrogen-ion concentration after each addition; this process is continued until the solution has a  $P_H$  value of 12.5. Then to an equal volume of water, proceeding in the same way, the same standard alkali is added until the same  $P_H$  value is obtained, care being taken to add sufficient water to give the blank the same volume as that of the original solution at the  $P_H$  value. Subtracting the number of c.c. used in the blank from that required in the original titration gives the number of c.c. of standard alkali necessary to neutralise the amino-acid alone. In this way it is possible to obtain the neutralisation curves of the amino-acids alone, and the influence of the different groups may be seen. Certain inaccuracies in the formalin titration method are explained by this method. An hydroxyl-ion concentration of about  $2 \times 10^{-2}$  ( $P_H=12.5$ ) will suppress the basic ionisation of the sodium salts of the amino-acids to a negligible extent, and thus make it possible to obtain a more exact quantitative estimation of the diamino-acids as well as of others containing strongly negative groups. J. F. S.

**Method of Graduating Ureometers of the Yvon Type.** CH. O. GUILLAUMIN (*J. Pharm. Chim.*, 1920, [vii], **21**, 342—346).—The ureometer is supported vertically with the tap at the lower end, and is filled with water; the open end is closed by a rubber stopper through which passes the end of a very narrow, graduated tube about 18 cm. long and having a capacity of 2 c.c. The ureometer is then turned so that the tap is at the top, the level of the water having been adjusted previously to the zero mark on the graduated tube, and small quantities of air are admitted successively through the tap, the volumes of these quantities being given by the changes in level of the water in the graduated tube. W. P. S.

**Braunstein's Modification of the Mörner-Sjöqvist Process for the Estimation of Urea.** ALAN HEREPATH TODD (*Biochem. J.*, 1920, **14**, 252—254).—This modification (A., 1901, ii, 140) does not give a quantitative yield of urea nitrogen. Ignition of the filtrate for fourteen hours at  $185^\circ$  with 15 grams of crystalline phosphoric acid gives an accurate result. J. C. D.

**Estimation of Uric Acid by a Modification of Blarez and Tourrou's Method.** G. PÉGURIER (*Ann. Chim. anal.*, 1920, [ii], **2**, 109—110).—Fifty c.c. of urine are treated with 5 c.c. of saturated sodium carbonate solution, and the mixture is added

slowly to 5 c.c. of Fehling's solution decolorised previously by the careful addition of sodium hydrogen sulphite solution. The precipitate which forms is collected on a filter, and washed with water; the filter and precipitate are then transferred to a beaker containing 150 c.c. of water and 10 c.c. of dilute sulphuric acid (1:1), and the mixture is titrated with 0.212% potassium permanganate solution. Each c.c. of the latter corresponds with 0.1 gram of uric acid per litre of urine.

W. P. S.

**Action of the Arsenotungstic Reagent on certain Alkaloids and Glucosides.** LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1916, **4**, 256—258).—The arsenotungstic reagent for phenolic groups proposed by Guglielmelli (A., 1916, ii, 584) has been applied to a large number of alkaloids and glucosides, and the result is tabulated in the original.

W. R. S.

**Forensic Investigation of Aconitine. Its Resistance to Putrefaction.** LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1918, **6**, 480—487).—A rat was killed by subcutaneous injection of 0.002 gram of aconitine. The carcase was left to putrefy seven days in the air, and subsequently buried during two months in a metal box. The pulped viscera were treated with absolute alcohol, slightly acidified with 10% tartaric acid, and kept for fifteen minutes at 50°; the cooled liquid was filtered and distilled in a vacuum; the residue was left overnight in contact with 250 c.c. of absolute alcohol, the liquid filtered, and distilled in a vacuum. This treatment was repeated twice. The final residue was dissolved with 200 c.c. of water, which was distilled off to remove alcohol, again dissolved in water, and filtered. This liquid was extracted in a separator (1) with ether, (2) with ether after previous addition of sodium hydrogen carbonate to feebly alkaline reaction, and (3) with chloroform. The last extract was evaporated and the residue treated with 10% acetic acid. It gave positive reactions with Mayer's and Monti's reagents, had the characteristic action on the tongue, and gave a violet coloration with a solution of 1 gram of sodium molybdate in 25 grams of phosphoric acid. Brouardel and Boutmy's reaction for ptomaine was negative. The conclusions are: that aconitine is not destroyed by the natural blood ferments; that it resists putrefaction for two months; that weak acids and alkalis should be used for its extraction; that its characterisation may be effected by the organoleptic test and the reaction with phosphoric acid and sodium molybdate; that crystallised aconitine does not give a violet coloration with official phosphoric acid, either hot or cold.

W. R. S.

**Test for Strychnine.** H. E. BUC (*J. Assoc. Off. Agric. Chem.*, 1919, **3**, 193).—One gram of zinc amalgam and 0.5 c.c. of hydrochloric acid are added to 0.5 c.c. of the strychnine salt solution; after fifteen minutes, the liquid is decanted and treated, drop by drop, with 0.02% potassium ferricyanide solution. A pink to rose-red coloration is obtained. The zinc amalgam is prepared by

washing granulated zinc with hydrochloric acid, treating it for one hour with 1% potassium antimonyl tartrate solution, and then adding mercuric chloride solution and a small quantity of hydrochloric acid; after thirty minutes, the zinc is removed from the solution, washed, and dried. The test will detect 0.001 mg. of strychnine provided that interfering substances, such as large amounts of other alkaloids and certain organic substances, are absent.

W. P. S.

**Use of Ethyl Acetate as a Precipitating Reagent for Proteins.**

A. MARIE (*Ann. Inst. Pasteur*, 1920, **34**, 159—161).—Ethyl acetate gives a marked precipitate with even dilute solutions of proteins, and a turbidity with peptones, proteoses, or albumoses, but solutions of amino-acids or vegetable or animal alkaloids show no apparent change in their physical state on its addition.

W. G.

**Important Source of Error in Investigating Urines for Albumin by means of Sulphosalicylic Acid.**

SCHALL (*Münch. med. Woch.*, 1920, **67**, 164—165; from *Chem. Zentr.*, 1920, ii, 582—583).—It is found that sulphosalicylic acid gives a precipitate with urines rich in calcium which may easily be mistaken for a positive albumin reaction. The distinction between precipitated calcium sulphate and albumin is most readily made if the urine is previously diluted with at least half its volume of water; under these conditions calcium sulphate is not precipitated, whilst the albumin reaction is but little affected.

H. W.

**Estimation of the Fibrin, Globulin, and Albumin Nitrogen of Blood Plasma.**

GLENN E. CULLEN and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1920, **41**, 587—597).—Fibrin is estimated by precipitation with calcium chloride under definite conditions from plasma containing 0.5% potassium oxalate. After thorough washing, the precipitate is submitted to the Kjeldahl process.

Albumin is estimated in plasma by precipitating the globulin by half saturation with ammonium sulphate, quantitatively removing the excess of ammonia in the filtrate, and making a Kjeldahl estimation on the residue. Non-protein nitrogen is estimated after removal of the plasma proteins by trichloroacetic acid. The plasma proteins are, therefore, separately estimated as follows: Fibrin N, directly; globulin N = total N - (filtrate N + fibrin N); albumin N = filtrate N - non-protein N.

J. C. D.

**Crystallisation of Hæmatoporphyrin.**

TH. LOCHTE and E. DANZIGER (*Vierteljahrsschrift ger. öffentl. Sanitätswesen*, **59**, 140—143; from *Chem. Zentr.*, 1920, ii, 396—397).—The method described depends on Willstätter's process, and is effected in the following manner. The spot of blood is removed as completely as possible and covered in a small test-tube with about 0.5 c.c. of hydrobromic-glacial acetic acid solution; the tube is corked and heated at 40—50° for about fifteen minutes. After remaining for thirty-six to forty-eight hours at the ordinary temperature, water

is added, followed by sodium hydroxide solution sufficient to neutralise the acid; the solution is faintly acidified with acetic acid and extracted two to three times with ether. The ether is allowed to evaporate slowly on a small watch-glass, the residue is washed into the centre of the glass with two or three drops of alcohol, and then treated with three to five drops of concentrated hydrochloric acid. The watch-glass is covered with a larger dish, and the solution is allowed to evaporate slowly; crystals generally form within one or two days.

H. W.

**Colorimetric Estimation of Stercobilin.** R. GOIFFON (*Compt. rend. Soc. Biol.*, 1920, **33**, 60; from *J. Pharm. Chim.*, 1920, [vii], **21**, 286—288).—Stercobilin, a reduction product of bilirubin, yields a red-coloured mercury compound which is soluble in dilute ammonia. To estimate stercobilin in fæces, 40 c.c. of a 10% faecal solution are heated for one hour at 50° with 5 c.c. of saturated mercuric chloride solution; the warm mixture is then treated with 2 c.c. of ammonia, diluted to 50 c.c., filtered, and the coloration of the filtrate compared with that of a standard. The latter may consist of a mixture of 100 c.c. of 10% cobalt chloride solution and 5 c.c. of potassium dichromate solution. The value 10 is suggested as a normal when the colorations of the test and standard solutions are of equal intensity.

W. P. S.

**Colloid-chemical Considerations regarding the Reductase Test for Milk.** EGON EICHWALD (*Zeitsch. Nahr. Genussm.*, 1919, **38**, 359—361).—It is pointed out that the colloids in milk may play a part in the methylene-blue test for reductase in milk, and preliminary experiments show that the finer the state of division of the colloids (proteins and fat), the slower is the rate at which the blue colour is destroyed.

W. P. S.

**Reduced Eosin and Potassium Persulphate.** LEÓN GOLDENBERG (*Anal. Soc. Quim. Argentina*, 1917, **5**, 264—266).—A colourless solution of reduced eosin may be obtained almost instantly and in the cold by weighing 1 gram of eosin, dissolving 2 grams of sodium hydroxide in 100 c.c. of water redistilled in glass, adding part of the eosin and 5 grams of chemically pure zinc dust, and shaking until decolorisation is complete. The remainder of the eosin is then added in portions whilst shaking. The stock solution thus obtained may be kept for two to three weeks, after which the eosin acquires a yellow colour on regeneration. For investigating oxydases, 0.5 c.c. of the above solution is made up to 100 c.c. The incomplete decolorisation of eosin by commercial zinc dust and distilled water condensed in metallic receivers is due to the presence of copper, traces of which are sufficient to induce catalytic re-oxidation of the reduced eosin.

The oxidising action of oxydases may be measured by comparison with a *N*/100-solution of potassium persulphate, 1 c.c. of which furnishes 0.00016 gram of oxygen. The quantity of oxydase which

causes reduced eosin to absorb 0.00016 gram of oxygen in one hour at 37° is called the "oxydasogenous unit." As the solutions in which oxydases are determined are generally too turbid for comparison with the standard regenerated by persulphate, the regenerated eosin obtained in the determination is best precipitated by 2% hydrochloric acid, collected on a double paper, washed with the acid, and redissolved on the filter in 2—3% sodium hydroxide. The clear filtrate may now be matched against the persulphate standard.

W. R. S.

**Quantitative Measurement of Lipase and Amylase in Pancreatic Juice.** H. MAUBAN (*Compt. rend. Soc. Biol.*, 1920, **83**, 130; from *J. Pharm. Chim.*, 1920, [vii], **21**, 355—357).—Two c.c. of 0.2% starch solution are placed in each of ten tubes, and to the first is added 1 drop of pancreatic juice, to the second tube 2 drops, and so on. The tubes and their contents are heated at 37° for five minutes, 0.25 c.c. of Fehling's solution is then added to each, and the mixtures are boiled for one minute, a small quantity of potassium ferrocyanide being added to prevent precipitation of copper. In this way is found the quantity of pancreatic juice necessary to produce sugar just sufficient to decolorise the measured quantity of Fehling's solution. Six or seven drops of normal pancreatic juice are usually required.

W. P. S.

**Estimation of Soil Acidity and Alkalinity by means of Indicators in the Field.** EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1920, **10**, 217—223).—The method of estimating the acidity or alkalinity of a soil in terms of  $P_H$  (A., 1919, i, 428) has been adapted for use in field tests, and a table has been constructed showing the reactions of the soil corresponding with the colour changes of a series of indicators, each of which overlaps the next in the scale. Passing from extreme acidity to extreme alkalinity, these indicators and their corresponding  $P_H$  values are: *Bromophenol-blue*, dull green, 3.5; brownish-green, 4.0; violet, 4.5; *methyl-red*, violet, 4.5; red, 5.0; orange, 5.5; yellow, 6.0; *bromocresol-purple*, yellow, 5.5; brownish-green, 6.0; violet, 6.5; purple, 7.0; *bromothymol-blue*, yellow, 6.0; greenish-yellow, 6.5; green, 7.0; blue, 7.5; *phenol-red*, yellow, 6.5; orange-yellow, 7.0; orange, 7.5; red, 8.0; violet-red, 8.5; *phenolphthalein*, colourless, 8.0; pale pink, 8.5; deep pink, 9.0; violet-red, 9.5. A definite quantity of the soil is shaken with neutral salt-free water, and the clear extract tested with successive indicators until one indicator shows an intermediate colour or the extreme colorations of two successive indicators overlap, and the corresponding  $P_H$  value is obtained from the table. By treating standard solutions of known ionic concentration and comparing the colorations with those given by soil extracts with the same indicators, specific acidities differing by a factor of  $\sqrt[5]{10}$  or 1.59 ( $P_H=0.2$ ) may be distinguished, but in practice values differing by a factor of  $\sqrt{10}$  or 3.16 ( $P_H=0.5$ ) are sufficiently accurate, since the reactions of the soil from different parts of the root of the same plant may differ by a factor of 10 or more.

C. A. M.

## General and Physical Chemistry.

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**Relation between the Refractivity and Density of Carbon Dioxide.** P. PHILLIPS (*Proc. Roy. Soc.*, 1920, [A], 97, 225—240).—The density and refractive index of carbon dioxide have been determined at 34°, under such conditions as allowed a gradual change in density from 0.73 gram/cm.<sup>3</sup> downwards, with the object of testing the validity of the Lorenz and Lorentz formula. The experiments were made by means of a small Fabry and Perot etalon, and the density values were deduced from the total amount of gas used and the volume of the containing vessel. From measurements with the mercury lines  $\lambda\lambda$  5790, 5461, and  $4358 \times 10^{-8}$ , it is shown that the reciprocal of the Lorenz and Lorentz constant is a linear function of the square of the density. For the wave length  $5461 \times 10^{-8}$ , the relation between the refractive index and the density is  $(\mu^2 + 2)\rho(\mu^2 - 1) = 6.581 + 0.1130\rho^2$ .

J. F. S.

**Maxwell's Relation between the Refractive Index and Dielectric Constant and a Method of Determining Ionic Charges in Crystals.** M. BORN (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1918, 604—613).—On the space-lattice theory of the author, it is shown that the product of the ionic charge and the wave-length of the lattice-vibration in diatomic crystals may be expressed by the difference  $D - n_r^2$ , where  $D$  is the dielectric constant and  $n_r$  the nearly constant value of the refractive index between the short- and long-wave infra-red specific frequencies ("Eigenschwingungen"). By comparison with the wave-lengths of the residual-rays ("Reststrahlen"), an approximation to the ionic charge is obtained which is in moderate agreement with that of the electrolytic ions.

J. R. P.

**Reflection Capacities and Dielectric Constants of Insulating Solids and Liquids.** H. RUBENS (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1915, 4—20).—The simple relation between reflecting capacity in the infra-red and the electric conductivity of metals deduced by Maxwell had been confirmed in previous experiments. The analogous relation between reflecting capacity and dielectric constant was confirmed in the case of twenty-five solid insulators with eight different wave-lengths in the infra-red. The insulating liquids examined exhibited an entirely different relation, which is explained by a theory due to Debye, that part of the abnormally high dielectric constant arises from the orientation of the electric dipoles assumed to exist in the molecules.

J. R. P.



**Reflection Capacity and Dielectric Constants of some Amorphous Substances.** H. RUBENS (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1916, 1280—1293).—Measurements made on fifteen amorphous substances, mainly glasses, led to the result that, for infra-red radiation of long wave-length, the reflection capacities are in close agreement with those calculated from Fresnel's theory from the dielectric constants for slowly varying fields. Anomalous dispersion in the region of Hertzian waves could not in any case be detected.

J. R. P.

**Optical Properties of some Crystals in the Long-wave Infra-red Spectrum. I. and II.** TH. LIEBISCH and H. RUBENS (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 198—219, 876—900).—I. The reflection capacity of doubly-refracting crystals between the wave-lengths  $22\mu$  and  $300\mu$ , and the connexion between the electric and optical properties were determined. The results enable the frequency and strength of the corresponding vibrations in the space-lattice to be calculated.

II. Forty-eight crystals of different systems, excluding triclinic, were examined in the manner described in the previous abstract. The positions of the optic axes in adularia and gypsum were determined for ten different wave-lengths, and the gradual change of these axes in the direction of the axes of greatest and least dielectricity was found to be in agreement with the electromagnetic theory.

J. R. P.

**Critical Study of Spectral Series. V. Spectra of the Monatomic Gases.** W. M. HICKS (*Phil. Trans.*, 1920, [A], 220, 335—468. Compare A., 1910, ii, 86; 1912, ii, 512; 1913, ii, 810; 1915, ii, 499).—A theoretical paper in which the series relationships in the spectra of neon, argon, krypton, xenon, and radium emanation are examined mathematically. A table of spectrum constants, in which the most important numerical factors are contained, is given in the paper. The value of the *oun* in the various cases is neon, 14·47013; argon, 57·9209; krypton, 249·536; xenon, 611·0100; and radium emanation, 1787·024.

J. F. S.

**Excitation of the Band Spectrum of Nitrogen by Electrons of Feeble Velocity.** LÉON BLOCH and EUGÈNE BLOCH (*Compt. rend.*, 1920, 170, 1380—1382).—From a spectrographic study under special conditions, it is shown that it is possible to excite the radiation of nitrogen with a critical potential of about 10 volts, the band spectrum thus being excited by electronic shock under a voltage decidedly lower than the potential of ionisation (18 volts).

W. G.

**Measurements of Wave-lengths in the Spectra of Krypton and Xenon.** PAUL W. MERRILL (*Bur. Standards, Bull.*, 1919, 15, 251—257; *Sci. Paper No.* 345).—This paper records photographic measurements of wave-lengths in the spectra of krypton and xenon,

principally in the red and infra-red. In krypton thirty-seven new lines were measured between 6576 Å and 8928 Å; in xenon fifty-two new lines between 6318 Å and 9162 Å. In this region there are numerous strong lines which are probably among the most important in the spectra of these elements. The xenon lines at 8231 Å and 8280 Å are especially notable. These and other lines may be of value as wave-length standards in the infra-red. Attention is called to a probable analogy between the spectra of the rare gases neon, argon, krypton, and xenon that this investigation has brought to light, which is shown in the tendency of the lines to form groups the position of which apparently has some relation to the atomic weight.

CHEMICAL ABSTRACTS.

**Absorption Spectra of Metal Ammine Complexes. III. Absorption Spectra of Complex Salts of Nickel, Chromium, and Copper.** YUJI SHIBATA and K. MATSUNO (*J. Coll. Sci. Tokyo*, 1920, **41**, 6, 1—37. Compare A., 1919, ii, 381; this vol., ii, 141).

—The absorption spectra of a large number of chromium complex amines, complex sulphates and oxalates, simple chromic salts and complex perchromic derivatives have been measured. Similar measurements have been made for nickel amines, simple nickel salts, complex pyridine copper derivatives, copper amines, and simple copper salts. The complex chromic compounds are shown to be stable in aqueous solutions and to give generally two or three sharp absorption bands. They are in every way comparable with the complex cobalt derivative as regards the absorption spectrum. The complex nickel compounds are generally unstable in aqueous solutions; the absorption spectra were, therefore, determined in ammoniacal solution. They exhibit, in every case, two absorption bands, but the absorption is much less strong than in the case of the metals previously examined. The absorption of the complex nickel compounds follows the same laws as that of the complexes of chromium and cobalt. The complexes of copper are the most labile in aqueous solution, and the anion exerts some influence on the absorption in this case. They give no bands, but there is general absorption in both the red and violet ends of the spectrum.

J. F. S.

**Ultra-violet Spectrophotometry of the Nitrophenols.** FRED VLÈS (*Compt. rend.*, 1920, **170**, 1242—1245).—The spectrum of the nitrophenols in the region studied,  $\lambda = 250 \mu\mu$  to the visible spectrum, is constituted in general by three elements, namely, (1) an absolutely constant *N*-band due to the absorption of the nitro-groups; this band appears to be formed by two components; (2) a band  $\phi$ , sometimes uncertain, due to the phenolic radicle; (3) a band  $\psi$ , inferior to the region studied, and the origin of which is problematical. The constitution in wave-lengths of the spectrum of a compound will be given by the characteristics of the isolated components, slightly modified by coefficients which will depend on the stereochemical properties of the compound. W. G.

**Absorption in Respect to the Properties of the Nitrophenols.** FRED VLÈS (*Compt. rend.*, 1920, 170, 1316—1318).—A continuation of previous work (preceding abstract) in which it is shown that it is possible to calculate the absorption spectrum curves of the nitrophenols simply from their constitution and the properties of their constituent groups. W. G.

**Abnormal Rotatory Dispersion.** G. BRUHAT (*Ann. Physique*, 1920, [ix], 13, 25—48).—The first part of the paper is a mathematical discussion of the general conditions which a spectropolarimeter should satisfy. The second part is a study of certain coloured tartrates, uranyl tartrate, didymium tartrate in ammoniacal solution, and the cobalt tartrates. The results obtained confirm Natanson's law and the law previously enunciated by the author (compare A., 1915, ii, 302, 503). W. G.

**Photochemical Activity of Absorbed Radiations.** CHR. WINTHER (*Danske Vid. Selsk. Math. Phys. Medd.*, 1920, 2, No. 3, 1—35; from *Chem. Zentr.*, 1920, i, 722).—The law of critical activity explains the peculiar fact observed by Warburg (this vol., ii, 210) that the "specific photochemical effect" is of the same order of magnitude for a series of very dissimilar processes. By its aid, the sensitiveness towards light of a particular reaction can frequently be approximately estimated when only its temperature-coefficient in darkness is known. It also affords a ready explanation of the generally observed small temperature-coefficients of photochemical processes and of their increase with increasing wave-length, and also indicates the possibility of chemi-luminescence. It possibly also explains the empirical observation that a process is more susceptible to optical sensitisation for a given wave-length when it is least sensitive to this wave-length. H. W.

**Energy-changes during Photochemical Reactions in Gases.**  
**IV. Influence of the Wave-length and Pressure on Photochemical Ozonisation.** E. WARBURG (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1914, 872—885. Compare A., 1911, ii, 834; 1912, ii, 315; 1913, ii, 652).—The amount of ozone produced in oxygen by ultraviolet light of wave-length  $0.253\mu$  is smaller, per calorie absorbed, than with light of wave-length  $0.209\mu$ . It is smaller under a pressure of 300 kg. per sq. cm. than under a pressure of 125 kg. per sq. cm. Both results are in contradiction to Einstein's law of photochemical equivalence, which requires considerable modification to accord with experiment. Of the original assumptions of Einstein, (1) that only one quantum is absorbed, (2) that all absorbing molecules are decomposed, the first may for the present be retained, but the second may be modified by assuming that only a portion of the absorbing molecules are decomposed. J. R. P.

**Energy-changes during Photochemical Reactions in Gases.** **V. Absorption of Ultra-violet Radiation by Oxygen.** E. WARBURG (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1915, 230—242).—Between pressures of 30 to 400 atm., large deviations

from Beer's law were found. The molecular absorption of oxygen increases appreciably with the pressure. The increase is greater for the shorter ( $0.209\ \mu$ ) than for the longer ( $0.253\ \mu$ ) of the waves used, and was greater in pure oxygen than in mixtures of oxygen and nitrogen. The deviations are explained by a theory of K. Ångström (*Arkiv. Math. Astron. Fysik*, 1908), according to which they are due to molecular collisions, and are represented by formulæ.

J. R. P.

**Energy-changes during Photochemical Reactions in Gases.**

**VI. Photolysis of Hydrogen Bromide.** E. WARBURG (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1916, 314—329).—The photolysis of hydrogen bromide by the wave-lengths  $0.209\ \mu$  and  $0.253\ \mu$  follows Einstein's law of photochemical equivalence; the photochemical action per unit of energy absorbed increases with the wave-length, and nearly in the ratio required by the theory. The law can hold only when the work required in the decomposition of the molecule is smaller than the quantum of the decomposing radiation. This relation is fulfilled with hydrogen bromide with the two wave-lengths used, but is not fulfilled in the photolysis of ammonia by the wave-length  $0.209\ \mu$  and of oxygen by the wave-length  $0.253\ \mu$ . The deviations found in the last two cases are therefore explained.

J. R. P.

**Energy-changes during Photochemical Reactions in Gases.**

**VII. Photolysis of Hydrogen Iodide.** E. WARBURG (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1918, 300—317).—The fulfilment of Einstein's law of photochemical equivalence was demonstrated with hydrogen iodide with the wave-lengths  $0.207\ \mu$ ,  $0.253\ \mu$ , and  $0.282\ \mu$ .

J. R. P.

**Energy-changes during Photochemical Reactions. VIII. Photolysis of Aqueous Solutions and the Law of Photochemical Equivalence.** E. WARBURG (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1918, 1228—1246).—Aqueous solutions of nitrates of alkalis and alkaline earths are converted by photolysis into nitrites. The specific photochemical action is considerably greater in weakly alkaline than in weakly acid solutions, increases with the concentration of nitrate, and is greater for shorter than for longer waves, in contradiction to Einstein's law of photochemical equivalence.

J. R. P.

**Energy-changes during Photochemical Reactions. IX. Photochemical Transition of Isomerides.** E. WARBURG (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 960—974).—The conversion of maleic into fumaric acid under the influence of wave-lengths  $0.207\ \mu$ ,  $0.253\ \mu$ , and  $0.282\ \mu$  in aqueous solutions was studied. The results indicated that the extension of the law of photochemical equivalence (see IV, this vol., ii, 404) does not lead to quantitative results, but serves as a guide to the theoretical interpretation of the experiments.

J. R. P.

**Photochemical Dissociation of Ferric Chloride.** ERNESTO PUXEDDU (*Gazzetta*, 1920, **50**, i, 154—161).—Exposure to direct sunlight of a dilute solution of ferric chloride in pure anhydrous ether results in almost instantaneous reduction of the salt to ferrous chloride. No reversion of this reaction occurs in the dark, the chlorine liberated during the reduction being completely used up, partly in chlorinating the ether, apparently to a mixture of the dichloro- and trichloro-derivatives, and partly in oxidation processes, with formation of aldehydes; the latter undergo polymerisation to some extent.

In moderately concentrated ethereal solution, ferric chloride is slowly reduced to a mixture of ferrous chloride and a brownish-black organic iron compound containing 2.8% of the metal, and only if this compound is gradually removed is complete reduction possible.

T. H. P.

**The Disruption of Atoms by  $\alpha$ -Rays.** G. S. FULCHER (*Science*, 1919, **50**, 582—584).—In Rutherford's recent papers on the nuclear bombardment of light atoms by  $\alpha$ -particles, he finds that the ranges of the swiftly accelerated nitrogen and oxygen atoms correspond fairly closely with those to be expected if the swift particles consisted of the singly charged nitrogen and oxygen atoms. The author points out that this requires that the other outriding electrons should accompany the parent atom in its swift motion, which is open to twofold objection. First, a velocity approaching  $10^9$  cm. sec.<sup>-1</sup> could not be imparted to the electrons in less than  $10^{-18}$  sec. The strength of the field not being great enough to overcome the inertia of the electrons, they would be left behind initially. Secondly, admitting that the first contention is wrong, the author believes that the outriding electrons would soon be brushed off by the large number of atoms encountered in the long range of flight. As an alternative, the possibility is suggested that the nitrogen atom, presumably composed of hydrogen and helium atoms, is entirely disrupted, and that the particles observed by Rutherford are really doubly charged helium atoms or  $\alpha$ -particles. The additional energy necessary to give them a range greater than that of the initial bombarding  $\alpha$ -particles would come from the internal energy of the atom in the moment of its disruption, and the phenomenon would constitute a type of artificially produced radioactivity. One difficulty of the author's assumption is to account for the large number of particles which take the same direction as the initial  $\alpha$ -particles. He believes this difficulty will not prove insurmountable. Examination of the  $e/m$  value of the particles will determine whether Rutherford is correct.

CHEMICAL ABSTRACTS.

**X-Ray Spectra of the Elements.** R. WHIDDINGTON (*Phil. Mag.*, 1920, [vi], **39**, 694—696).—A theoretical paper in which the speed of the electron ( $v$ ) carrying the same energy as the  $\alpha$ -lines in the  $K$  and  $L$  spectra of the elements is shown to be fairly well represented by the formula  $v = C \cdot N + D$ , where  $N$  is the atomic

number of the element and  $C$  and  $D$  are constants determined by the series. For the  $K$  series  $v=2(N-2)10^8$  cm./sec., and for the  $L$  series  $v=(N-15)10^8$  cm./sec. The values of  $v \times 10^{-8}$  and  $2(N-2)$  and  $v \times 10^{-8}$  and  $(N-15)$  are compared, respectively, in the  $K$  series (nine elements) and in the  $L$  series (seven elements), when a very fair agreement is obtained. J. F. S.

**The Fine Structure of X-Ray Spectra.** M. DE BROGLIE (*Compt. rend.*, 1920, **170**, 1245—1246).—As in the case of the X-ray spectrum of tungsten (compare this vol., ii, 344), it is found that the rhodium spectrum contains a ray which really consists of two components, for which  $d\lambda=0.0006$  Ångström. W. G.

**Spectrum of X-Rays from an Aluminium Target.** W. DUANE and TAKEO SHIMIZU (*Physical Rev.*, 1919, **14**, 389—393).—The general radiation spectrum of aluminium for wave-lengths from  $0.1820 \times 10^{-8}$  to  $1.259 \times 10^{-8}$  cm. has been carefully examined for characteristic radiation which might belong to the  $J$ -series of short wave-lengths found by Barkla. No characteristic radiation was found that could not be attributed to molybdenum from the tube or lead from the jaws of the slit. CHEMICAL ABSTRACTS.

**X-Ray Absorption Frequencies Characteristic of the Chemical Elements.** WILLIAM DUANE and KANG-FUH-HU (*Physical Rev.*, 1919, **14**, 516—521).—The critical absorption frequencies in the  $K$ -series for the elements from bromine ( $N=35$ ) down to manganese ( $N=25$ ) were measured. Using these and other data, it is shown that for the elements from cerium to magnesium the square root of the critical frequency is not quite a linear function of the atomic number,  $N$ . The deviations amount to several units %. However, the critical velocities, calculated from the quantum relation  $\frac{1}{2}mv^2 = h\nu$ , using the transverse relativity mass  $m = m_0[1/\sqrt{1-(v/c)^2}]$ , are found to be linear with  $N$  to within about one-fifth %. CHEMICAL ABSTRACTS.

**X-Ray Absorption Frequencies Characteristic of the Chemical Elements.** W. DUANE and TAKEO SHIMIZU (*Physical Rev.*, 1919, **14**, 522—524).—The measurements of critical  $K$  absorption frequencies for the elements from lead ( $N=82$ ) to neon ( $N=60$ ) were made. The deviation from linearity of the sq. root of the frequency with  $N$  is much greater than for the lighter elements. This is also true of the deviations of the critical velocity as measured by Duane and Kang-Fuh-Hu (preceding abstract). CHEMICAL ABSTRACTS.

**Relation between the Intensity of General X-Radiation and the Atomic Number of the Anticathode.** W. DUANE and TAKEO SHIMIZU (*Physical Rev.*, 1919, **14**, 525—529).—The intensity of the general X-radiation from the four elements iron, cobalt, nickel, and copper was measured and found to be proportional to the atomic number rather than to the atomic weight.

These four elements were chosen because, in the case of nickel and cobalt, the atomic weight and atomic number are in reverse order.

#### CHEMICAL ABSTRACTS.

**Crystallisation of a Radium Barium Solution.** CLARENCE E. SCHOLL (*J. Amer. Chem. Soc.*, 1920, **42**, 889—896).—Crystallisation of the systems radium chloride-barium chloride and radium bromide-barium bromide are considered theoretically, and a number of experiments based on the theoretical results described. On cooling a saturated solution of the chloride from 100° to 0°, one-half of the total chlorides separates, whilst one-third of the bromides separate under similar conditions. The concentration of radium in any dish in the positive direction is given by  $C = AK^n$ , where  $C$  is the concentration,  $A$  the known concentration of the dish at the start,  $K$  the factor of enrichment, and  $n$  the number of recrystallisations. The concentration of any dish in the negative direction is  $C' = A'(X - K)^m / (X - 1)^m$ , where  $X$  is the inverse fractional proportion of the total weight of material occurring as crystals, and  $m$  the number of crystallisations in the negative direction. In the case of the chlorides, 50% of the material separates from 0.5*N*-hydrochloric acid solution, which gives a factor of enrichment of 1.62. Hence  $C = A \times 1.6^n$  and  $C' = A \times 0.4^m$ . Crystallising so that the crystals move one dish forward and the liquors two dishes backward, a concentration is effected as follows: if 1.0 be the radium concentration of the starting dish, that of the fifth dish to the right has a concentration of 10.6, whilst the eighth dish to the left has a concentration of 0.026. In the bromide system, one-third the material separates from saturated solutions of 0.33*N*-hydrobromic acid, and the enrichment factor is 2.49. Hence  $C = A \times 2.49^n$  and  $C' = A \times 0.25^m$ . Crystallising so that the crystals go two dishes to the right and the liquors three dishes to the left, the following concentration is obtained. If the radium concentration in the starting dish be 1.0, then the ninth dish to the right has a concentration of 62, and the ninth dish to the left has a concentration of 0.016. Hence the bromide system is more efficient than the chloride system. Several other systems are described.

J. F. S.

**Concentration of Radium and Mesothorium by Fractional Crystallisation.** JOHN L. NIERMAN (*J. Physical Chem.*, 1920, **24**, 192—200).—A number of crystallisations of barium bromide containing radium bromide and mesothorium bromide have been carried out in neutral solutions and in solutions in hydrobromic acid of various concentrations with the object of ascertaining the conditions under which the optimum crystallisation factor is obtained. By crystallisation factor, the author understands the ratio of radioactive bromide in the crystals to that in the substance before crystallisation. The results show that this factor is independent of the concentration of the hydrobromic acid. The crystallisation factor is given for various percentages of salt separating; thus, when 24.3% of the salt separates, the factor is

2.43, and this decreases with increasing separation to 1.44, when 69.0% separates. For concentrations of mesothorium up to 2 mg. per gram of salt, the crystallisation factor remains constant. The separation of mesothorium and radium from barium can be carried out advantageously in either neutral or dilute acid solutions of the bromides. All measurements of activity were made by means of the  $\gamma$ -ray. J. F. S.

**The Conductivity of Permutite Mixtures.** V. ROTHMUND and G. KORNFELD (*Zeitsch. anorg. Chem.*, 1920, 111, 76—77).—Polemical. A reply to A. Günther-Schulze (A., 1919, ii, 490). E. H. R.

**Form of the Conductivity Function in Dilute Solutions.** **Correction.** C. A. KRAUS (*J. Amer. Chem. Soc.*, 1920, 42, 990—991. Compare this vol., ii, 217).—Several of the equations previously published have been corrected. J. F. S.

**Electrolytic Potential of the Change Nitrite  $\rightarrow$  Nitrate + Nitric Oxide. The Energetic Relationships of the Most Important Compounds of Nitrogen with Oxygen and Hydrogen.** HANS PICK (*Zeitsch. Elektrochem.*, 1920, 26, 182—196).—A theoretical paper in which it is shown that the normal potential of the change  $2\text{NO}_2' \rightarrow \text{NO} + \text{NO}_3'$  at  $25^\circ$  may be calculated from the electrometric measurements of Moore (A., 1913, ii, 467), and the value +0.49 volt obtained. This value is also obtained from the chemical measurements of the equilibrium of the decomposition of silver nitrite (Abegg and Pick, A., 1906, ii, 833). Using this normal potential, the equilibrium measurements of Lewis and Edgar (A., 1911, ii, 264) for the chemical decomposition of nitrous acid into nitric oxide and nitric acid, the energetic relationships between the substances  $\text{NO}_3'$ ,  $\text{NO}_2'$ , NO, and  $\text{HNO}_2$  are calculated for  $25^\circ$ , and the results expressed as normal potentials. From thermodynamic relationships and from equilibrium data previously published, the energetic relationships are deduced and expressed as normal potentials for the substances  $\text{N}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{NH}_4^+$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_4$ . The normal potentials thus calculated are compared with known chemical and electrochemical data and found to be in good agreement. J. F. S.

**Photoelectric Investigations with Salt Solutions.** TORSTEN SWENSSON (*Arkiv. Kem. Min. Geol.*, 1917, 7, No. 19, 1—142).—The change of *E.M.F.* occasioned by illuminating one side of a cell, of the type  $\text{Pt}|\text{soln.}||\text{soln.}|\text{Pt}$ , by ultra-violet light whilst the other half is dark, has been measured for solutions of potassium and cobalt chlorides, cobalt ammonium sulphate, nickel, cobalt, manganese, chromium, zinc, magnesium, copper, and potassium sulphates, sulphuric acid, hydrochloric acid, mixtures of potassium dichromate and sulphuric acid, potassium ferricyanide and potassium hydroxide, and potassium ferrocyanide, potassium ferri-cyanide, and potassium hydroxide. All measurements were made



over prolonged intervals, and the solutions were stirred by a fine stream of nitrogen. The measurements were made both with the electrode illuminated and unilluminated. It is shown that in most cases the *E.M.F.* towards an indifferent electrode changes on illumination. The change depends on the nature of the salt, and after the illumination ceases, the *E.M.F.* changes in the direction of the value which the solution previously possessed. Both positive and negative changes of *E.M.F.* are observed, and, in consequence, maxima and minima, as well as inflexion points, are found in the potential-time curves. The theoretical formula

$$E = \rho kLB / (kL + k_1) [1 - e^{-(kL + k_1)t}] - \rho k_2 L_1 B_1 / (k_2 L_1 + k_3) [1 - e^{-(k_2 L_1 + k_3)t}]$$

has been tested by the results obtained with the simple salt solutions and found to be generally obeyed. The nitrogen used is shown to have no other effect than that of a stirrer, and the photo-electrical effect is shown not to be due to the formation of ozone or hydrogen peroxide. The illumination of the electrode is also unnecessary for the production of the potential change. In the case of nickel sulphate, the effect of the light intensity is shown to be in accordance with the formula

$$E = \rho kLB / (kL + k_1) [1 - e^{-(kL + k_1)t}].$$

The effect is either proportional to the concentration or entirely independent of the concentration, depending on the relationship between the concentration and the intensity of illumination. Experiments with mixtures of potassium dichromate and sulphuric acid showed that the potential increased on illumination, whilst with the substances alone it decreased. In the mixtures, the effect was at first negative, but soon changed to a strong positive effect. Here also the illumination of the electrode is without effect, and the change of *E.M.F.* is occasioned by the ultra-violet light waves, which are absorbed by glass. The change of *E.M.F.* in these cases is independent of the concentration, but depends on the composition of the mixture, the maximum effect being obtained with a solution containing 75 mols. % of potassium dichromate. The *E.M.F.* returns to the original value when the light is removed with a velocity which depends on the composition of the solution, and is greatest for pure sulphuric acid. Solutions of potassium ferrocyanide in alkaline solution, on illumination showed at first a decreased *E.M.F.*, which rapidly changed to an increased value. In mixtures of ferrocyanide and ferricyanide in alkali, the velocity of the change of potential is greater the larger the amount of ferricyanide present. Experiments with Röntgen rays gave an effect of the same nature, but much smaller than that observed with ultra-violet light. Theories are put forward to explain the effects observed. An historical summary of the work already published on this subject is included in the paper.

J. F. S.

**The Theory of Electrolytic Ions. XIV. Kohlrausch's Law of Additivity.** RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1920, **111**, 55—75).—The work of Bjerrum (*A.*, 1919, ii, 9) and

others indicates that strong electrolytes in dilute solution are completely dissociated. The molecular conductivity,  $\mu$ , can be expressed by the equation  $\mu = \alpha F(U + V)$ , where  $\alpha$  is the degree of dissociation,  $F$  the constant of Faraday's law, and  $U$  and  $V$  the ion mobilities, which are supposed to be invariable. Since the conductivity,  $\mu$ , with decreasing concentration approaches a limiting value,  $\mu_0$ , it follows that, if dissociation is already complete,  $U$  and  $V$  must be variable, and must approach limiting values,  $U_0$  and  $V_0$ . A new equation is obtained,  $\mu = F(xU_0 + yV_0)$ , where  $x$  and  $y$  are mobility coefficients. According to the old theory, the transport number,  $n$ , is given by  $n = U/U + V$ , and is a constant, independent of the degree of dissociation,  $\alpha$ . In terms of the new theory, however, where, instead of variable degree of dissociation, variable ionic mobility is assumed, the transport number also becomes variable, namely,  $n = xU_0/(xU_0 + yV_0)$ . The transport numbers can only be equal when the mobilities of the two ions (in the case of electrolytes dissociating into two simple ions) are equal, for it is shown that the rate of change of mobility with concentration is the same for all ions. In the cases of potassium chloride, bromide, and iodide, the mobilities of all the ions are approximately equal at the same concentration, and consequently the transport numbers are practically constant for all concentrations. The mobilities and transport numbers of the ions have been recalculated for the salts potassium chloride, bromide, iodide, nitrate, nitrite, chlorate and thiocyanate, and sodium chloride, nitrate and iodate, and the values of the mobility-coefficients of the potassium, sodium, and chlorine ions at different concentrations are tabulated.

E. H. R.

**Cadmium-Vapour Arc Lamp.** HENRY J. S. SAND (*Phil. Mag.*, 1920, [vi], 39, 678—679).—An answer to Bates's criticism of the cadmium vapour arc lamp (this vol., ii, 221). The author points out that the difficulties experienced were due in all probability to faulty pumping and to the presence of oxide formed by traces of water vapour.

J. F. S.

**Investigation of Mewes' Law of the Relation between the Volume of a Gas and the Temperature.** RUDOLF MEWES (*Zeitsch. Sauerstoff Stickstoff Ind.*, 1920, 12, 10—13; from *Chem. Zentr.*, 1920, i, 694—695).—In continuation of previous investigations (this vol., ii, 227), the author shows that the assumptions underlying the considerations of ideal gases are no longer tenable, and must be replaced by new hypotheses. The experiments, which disprove the older ideas, confirm the equations which have been proposed by him.

Gay-Lussac's law is only valid for nitrogen at the atmospheric pressure, and does not hold for increased or decreased tensions. Conversely, the discrepancies from Mewes's summation law increase greatly with increasing initial pressure. It is found that this phenomenon can be explained by a consideration of the effects of surface condensation and the action of mass. The influence of

surface condensation and partial liquefaction becomes less marked as the tension to which the gases are brought by cooling decreases. For this reason, the densities of gases at low temperatures can be most accurately estimated by observing the change of tension with diminishing temperature, as has been demonstrated by a series of unpublished experiments.

H. W.

**Specific Heat of Saturated Vapour and the Entropy Temperature Diagrams of certain Fluids.** (Sir) J. A. EWING (*Phil. Mag.*, 1920, [vi], **39**, 633—646).—A theoretical paper in which the change in the value of the specific heat of a saturated vapour,  $K_s$ , with temperature is considered. In the case of steam the value is negative, whilst with ether it is positive. It is shown that  $K_s = Td\phi_s/dT$ , where  $\phi_s$  is the entropy of the saturated vapour, and consequently the value of  $K_s$  is negative under all conditions that make the entropy of the vapour increase with decreasing temperature. It is negative so long as the entropy temperature line for saturated vapour slopes down to the right; this form of curve is found for steam, carbon dioxide, and ammonia, and may be termed the normal curve. If the curve slopes in the opposite direction, the value of  $K_s$  is positive, and this type of curve is found for ether, benzene, ethyl propionate, and acetic acid. The entropy-temperature diagrams are drawn from known data for ethyl alcohol, propyl alcohol, ethyl ether, benzene, ethyl propionate, and acetic acid.

J. F. S.

**Specific Heats and Heats of Fusion of the Dichloro-, Chlorobromo-, Dibromo-, Bromiodo-, and Diiodobenzenes. Correction.** J. NARBUTT (*Zeitsch. Elektrochem.*, 1920, **26**, 203—204).—A long list of corrections of formulæ and numerical data which occur incorrectly in the author's papers on the above-named subject (A., 1919, ii, 215, 216, 217).

J. F. S.

**Vapour Pressure and Heat of Vaporisation.** J. J. VAN LAAR (*Rec. trav. chim.*, 1920, **39**, 371—410. Compare this vol., ii, 287).—A theoretical, mathematical discussion of these two physical properties.

W. G.

**Surface Condensation Error in certain Measurements of Vapour Pressure by the Gas Current Saturation Method.** ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1920, **42**, 978—985).—The condensation of water from its saturated vapour in air on a water-washed and steamed glass surface and on an acid-washed, steamed, and water-washed asbestos surface has been investigated under the conditions which generally obtain in the use of the gas-current saturation method of vapour-pressure measurement. In the case of glass wool, the condensation amounts to 0.012—0.127 mg. per sq. cm. of glass surface at 22°, whereas asbestos takes up about 28—32% of the water from the saturated air. This quantity of deposited water is sufficiently large to explain the many un-

explained irregularities recorded in the literature of measurements of vapour pressure by this method. J. F. S.

**The Manipulation of Volatile Substances. IV.** ALFRED STOCK [with ERNST KUSS and KARL SOMIESKI] (*Ber.*, 1920, **53**, [B], 751—758. Compare A., 1914, ii, 171; 1917, ii, 442; 1918, ii, 353).—In the estimation of tension in the vacuum apparatus, it should be noted that a certain amount of fractionation occurs in the case of mixtures, whereby the vapour becomes richer than the residue in the volatile constituent. This factor is particularly important when only small quantities of material are available; undue reduction in the size of the apparatus is impracticable, and the experimental results must be interpreted with caution. In estimating the tension of solid substances, it is better to cool the regulating bath to the required temperature or to warm the substance somewhat above the experimental temperature before bringing it into the bath; with the reverse procedure, the temperature only becomes slowly uniform throughout the mass, and the tension registered is that of the coldest portion of the substance.

Fractional distillation is only advantageous in dealing with liquid substances. Solids should therefore be distilled under such pressure that they first liquefy. The receiver should be so cooled that a difference in tension of only a few millimetres exists between the substance under distillation and the distillate. Constant movement of the liquid is advisable, and for this purpose a special apparatus is described and figured; this consists essentially of a small induction coil with a simple interrupted and oscillating core. It is attached to the apparatus in the neighbourhood of the distillation vessel, and keeps the whole apparatus, and therefore the liquid, in steady vibration.

The Gaede rotary mercury-air pump previously used is now replaced by the Volmer mercury vapour pump, a Gaede rotary oil pump being used as accessory, whilst the gases are drawn off by an automatic Töpler pump. An improved automatic valve for use in connexion with the latter is described and figured.

The provision of suitable cooling baths for temperatures slightly above that of liquid air has previously been a matter of difficulty; it is now found that liquid propylene (b. p.  $-48^{\circ}$ ) fulfils the required conditions admirably, since it has an extraordinarily low melting point and remains highly mobile at the temperature of liquid air; a disadvantage, however, lies in its gaseous nature at the ordinary temperature. The direct introduction of liquid air into the cooling liquids is to be avoided, on account of the violence of its evaporation and also the unevenness of the induced cooling; the latter drawback is also noticed with baths in which the liquid air is allowed to evaporate in coils immersed in the cooling liquid. A special type of cooling vessel is figured which avoids these disadvantages; the liquid air is brought into a copper cylinder immersed in the cooling bath. Its effect is controlled and uniform, since cooling occurs from above downwards, whilst the metal tends

to equalise the temperature. For extremely low temperatures, the use of a heavy, cylindrical aluminium block is recommended; in this, four holes are bored. One of these serves for the introduction of liquid air, and, to avoid the spurting of the latter, is shielded from the remainder by a vulcanite partition. The remaining holes are used for the insertion of thermometers, substance under investigation, etc. The block may be insulated by being suspended in a Dewar vessel. By regulation of the pressure of the air, the temperature of the block may be kept constant to within a fraction of a degree for long periods. Equalisation of temperature between the metal and the thermometers, etc., may be hastened by filling the holes with liquid propylene, but this is only necessary in the case of extremely accurate experiments. The use of aluminium is particularly advantageous, since at low temperatures the metal has a low specific heat and an extraordinarily high conductivity for heat.

H. W.

**Thermal Capacity of Water between 5° and 50°.** W. JAEGER and H. VON STEINWEHR (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1915, 424—432).—The 15° calorie is found by refined electrical heating measurements to be equivalent to 4.184 international watt-seconds. The minimum specific heat of water occurs at 33.5°.

J. R. P.

**The Properties of Fluids in the Neighbourhood of the Critical Point and the Characteristic Equations.** G. BRUHAT (*Compt. rend.*, 1920, 170, 1173—1175).—A mathematical discussion of the subject, with special reference to the equations of van der Waals and Clausius.

W. G.

**Absolute Entropies of Monatomic Substances.** MAX PLANCK (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1916, 653—667).—From the equations of statistical mechanics, the characteristic thermodynamic functions are derived for a single atom moving freely in a hollow sphere and in a hollow, rectangular parallelepiped. The calculation is then extended to a monatomic gas, and it is shown that the degrees of freedom corresponding with the separate atoms must be incoherent. The expression of Nernst (*Verh. Deut. Physikal. Ges.*, 1916, 18, 83) for the energy of a gas is discontinuous in respect of temperature, so that a definite value of the specific heat cannot be found. Those deduced by Stern and Tetrode are identical with that found in the present paper, with the exception of an additive constant.

J. R. P.

**Relationships between Critical Data and other Properties of Organic Liquids.** W. HERZ (*Zeitsch. anorg. Chem.*, 1920, 111, 52—54. Compare A., 1920, ii, 285).—It has been shown that, for a large number of non-associated organic compounds, the quotient of the critical temperature,  $T_k$ , and the critical pressure,  $p_k$ , divided by the sum of the valencies of the constituent atoms ( $C=4$ ,  $H=1$ ,  $O=2$ , and  $N=3$ ), is approximately a constant, 0.45.

From the known relationship between critical volume, temperature, and pressure, it follows that  $v_k/z = \text{const.}$ , where  $v_k$  is the critical volume and  $z$  the sum of the valencies. This is shown to be the case for a number of esters, ethers, and hydrocarbons, the value of the constant varying between 0.00038 and 0.00047. It is also deduced that the value of the heat of vaporisation,  $L$ , can be found from the expression  $L = T_s/0.45d_kz$ , where  $T_s$  is the boiling temperature (abs.) and  $d_k$  the critical density. The molecular refraction,  $MR = 1.8T_k/p_k$ , can be written  $MR = 0.8z$ . Since, however, the molecular refraction depends also on the constitution of the compound, the values calculated from the formula are only approximate.

E. H. R.

### Comparative Method for Determining Vapour Densities.

PHILIP BLACKMAN (*J. Physical Chem.*, 1920, **24**, 225—229).—Two glass bulbs made of graduated burette tubing and about 10 cm. long are joined together by capillary tubing. The free ends are narrowed and drawn out into tubes of sufficient diameter to admit small weighing tubes. The apparatus is placed upright and half filled with mercury. The substances the vapour densities of which are to be compared are weighed out in very small quantities (0.02—0.10 gram) in narrow glass tubes and placed one in each bulb. One of the bulbs is then sealed at the top, and, when cooled to a known temperature, the difference in the height of the mercury levels is noted and the positions of the mercury level also noted, so that later the volume of air ( $V$ ) in the sealed bulb may be determined. The other bulb is then sealed, and the same measurements of mercury levels again taken, so that the volume of air ( $V_1$ ) may be determined. The apparatus is now placed in a deep beaker, covered with a suitable liquid, and heated to a temperature sufficiently high to vaporise completely both liquids. Again the mercury levels are determined, so that  $v_1$  and  $v_2$ , the volume of air and vapour in the two tubes, may be determined. The apparatus is now inverted, and the graduated tube cut away from the horizontal connecting tube, and the volumes,  $V$ ,  $V_1$ ,  $v_1$ , and  $v_2$ , determined by filling with mercury from an accurate burette to the observed levels. Four approximate formulæ for calculating the vapour density are given, which are applied to measurements with acetone, diethyl ether, chloroform, and ethyl alcohol. The results are very good.

J. F. S.

**Some Consequences of the so-called Deterioration Theory of Gases.** W. NERNST (*Sitzungsber. Preuss. Akad. Wiss., Berlin*, 1919, 118—127).—At very low temperatures, the ordinary gas law,  $pV = RT$ , is replaced by the equation  $p = (R/V) \cdot \beta\nu / (1 - e^{-\beta\nu/T})$ , where  $\beta = 4.863 \cdot 10^{-11}$ ;  $\nu = hN^{\frac{2}{3}}/4\pi mV^{\frac{1}{3}}$ , where  $N = 6.17 \cdot 10^{23}$ ,  $h = 6.55 \cdot 10^{-27}$ ,  $m$  = mass of molecule. For  $T = 0$ , this leads to a pressure at the absolute zero,  $p = h^2N^{\frac{2}{3}}/4\pi mV$ . This pressure is assumed to be due to directed repulsive forces analogous to valency acting between the molecules, which are inversely proportional to

the cubes of the distances. These will be appreciable only at extremely small distances, that is, at very low temperatures. The theory leads to the following equation for the viscosity at very low temperatures,  $\eta = m^3 u^3 / 9h^2$ , where  $u$  is the molecular velocity. The connexion between viscosity and temperature required by the theory is approximately fulfilled by the measurements on hydrogen at the lowest temperatures. The result is an indirect confirmation of the "deterioration theory" proposed by the author. J. R. P.

**Compressibility and Viscosity of Water and of its Solutions, and its Polymerisation.** STEFANO PAGLIANI (*Gazzetta*, 1920, **50**, i, 186—194).—The author discusses the work of Richards and Palitzsch (A., 1919, ii, 97), Pagliani and Palazzo (*Atti R. Accad. Sci. Torino*, 1884, **19**), Pagliani and Vicentini (*Mem. Accad. Lincei*, 1884, **19**), Pagliani (*Rend. R. Accad. Lincei*, 1889, **5**), Tait (*Proc. Roy. Soc. Edin.*, 1882, **12**), Tammann (A., 1910, ii, 495), van Laar (A., 1900, ii, 189), Bousfield and Lowry (A., 1910, ii, 842), Battelli (*Atti R. Accad. Sci. Torino*, 1885, **20**), and Pagliani and Oddone (*Atti R. Accad. Sci. Torino*, 1887, **112**), and draws the conclusion that the hypothesis of the polymerisation of water serves to explain most of the observations made on water and aqueous solutions with reference to their compressibility and viscosity, and to the variations of these with change of temperature, pressure, and concentration of the solutions. T. H. P.

**The Viscosity of Colloidal Solutions.** PAUL BARY (*Compt. rend.*, 1920, **170**, 1388—1390).—If a unit volume of dry colloid is swollen by a volume,  $\alpha$ , of liquid, Einstein's formula for the viscosity may be written  $\alpha = (\eta - 1 - 2.5v_0) / 2.5v_0$ , where  $\eta$  is the viscosity of the colloidal solution, that of the pure medium being taken as unity, and  $v_0$  is the amount of colloid in unit volume. This gives a means of determining the coefficient of swelling by viscosity measurements. It is shown that colloids which enter into suspension in a given medium without any external agency yield liquids in which the colloid shrinks progressively with the time to a degree which depends on the concentration and the temperature. This shrinking is accentuated by dilution, and tends towards zero for zero concentration. W. G.

**Adsorption of Hydrogen by Quartz at Low Temperatures.** G. R. PARANJPE (*Proc. Asiatic Soc. Bengal*, 1919, **15**, cxxxvi—cxxxvii).—An apparatus based on the principle of the differential manometer was used. Differences in pressure due to unequal adsorption in the two bulbs were measured by the volume change necessary to re-establish equilibrium. The measurements were made at  $-190^\circ$  and at pressures from 25 to 350 mm. The volumes of hydrogen adsorbed at these pressures by 100 sq. cm. of quartz surface, corrected to normal temperature and pressure, were 2.0 c. mm. and 10.5 c. mm. respectively. The results were used in calculating the correction for a hydrogen thermometer of quartz.

Even at this low temperature the correction is very small. Work with other gases and at other temperatures is in progress.

CHEMICAL ABSTRACTS.

### Adsorption of Sulphur Dioxide by the Gel of Silicic Acid.

JOHN MCGAVACK, jun., and W. A. PATRICK (*J. Amer. Chem. Soc.*, 1920, **42**, 946—978).—The adsorption of sulphur dioxide by silicic acid gels has been measured at 100°, 80°, 57°, 40°, 30°, 0°, -33·4°, -54°, and -80°. The effect of the water content of the gel was determined by using gels containing 2·31, 3·51, 4·86, and 7·97% of water respectively. It is shown that the maximum adsorption is exhibited by gels containing about 7% of water. The adsorption is shown to be reversible in all cases in the absence of air. In the presence of small amounts of air, the rate of adsorption was greatly decreased, and adsorption and desorption were irreversible. The empirical equation of Freundlich was found to hold over almost the entire range studied, exceptions being at those points where the saturation pressure was approached. The equation  $V/\sigma^{1/n} = K(p/p_0)^{1/n}$  is found to hold, where  $V$  is the uncorrected volume of the condensed phase,  $\sigma$  the surface tension,  $p$  the pressure of the gas phase,  $p_0$  the vapour pressure of the liquid, and  $K$  and  $1/n$  constants dependent on the physical properties of the adsorbent.

J. F. S.

**Sorption of Vapours by Charcoal.** BROR GUSTAFSON (*Arkiv. Kem. Min. Geol.*, 1917, **7**, No. 22, 1—17).—The sorption of vapours of water and acetic acid by charcoal has been examined at a series of pressures (4·6—17·4 mm.) and at temperatures 16·5—20°. In the case of water vapour, it is shown that for small pressures the amount of sorption is proportional to the pressure, and the sorption in these cases must consist in the formation of a solid solution; at pressures from 6—7 mm., the strict absorption commences. On producing the solution and absorption curves, they cut at a pressure 7·4 mm. The sorption velocity is greatest at the commencement, and decreases as the equilibrium conditions are approached; it is also greater at the lower pressures than at the higher pressures. In the case of acetic acid, much the same results are observed, but here an hysteresis occurs. The saturation pressure is greater when reached from above than when reached from below. This is held to be due to the two processes, solution and absorption, occurring simultaneously.

J. F. S.

**Electrolytic Conductivity in Non-aqueous Solutions. IV. The Solvation of the Ions of *p*-Tolyltrimethylammonium Iodide in a Number of Organic Solvents.** HENRY JERMAIN MAUDE CREIGHTON (*J. Franklin Inst.*, 1920, [5], **189**, 641—643. Compare A., 1919, ii, 44).—Walden's formula (this vol., ii, 230) is used to calculate the solvation of the ions of *p*-tolyltrimethylammonium iodide in a number of solvents. The molecular weight of the solute will be increased above the normal value, corresponding with Walden's equation, if solvation occurs. The solvation



values obtained with the solvents were: propaldehyde, 7.73; epichlorohydrin, 3.44; ethyl alcohol, 3.30; methyl alcohol, 2.91; benzaldehyde, 2.88; anisaldehyde, 2.21; propionitrile, 1.44; acetone, 1.29; nitromethane, 0; benzonitrile, 0; nitrobenzene, 0. Since Walden has shown that the iodide ion is not solvated in methyl alcohol, ethyl alcohol, acetone, and nitrobenzene, the above values probably represent the degrees of solvation of the organic cation. The tendency to solvation in aldehydes decreases with increase in the molecular weights of the latter.

J. R. P.

**Tabulation of Hydrogen- and Hydroxyl-ion Concentrations of some Acids and Bases.** ARTHUR W. THOMAS (*J. Amer. Leather Chem. Assoc.*, 1920, 15, 133—146).—The hydrogen-ion concentrations of the following acids are given for concentrations from 0.001*M* to 2*M*: acetic, boric, butyric, carbonic, citric, formic, gallic, hydrochloric, lactic, nitric, oxalic, phosphoric, salicylic, sulphuric, and tartaric. The hydroxyl-ion concentrations of ammonium, barium, calcium, potassium, and sodium hydroxides are also given. The values for the weak acids were calculated from Ostwald's dilution law, and for the strong acids from curves constructed from data in the literature. CHEMICAL ABSTRACTS.

**Surface Energy of Crystals and its Influence on the Crystalline Form.** M. BORN and O. STERN (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 901—913).—A mathematical paper in which the surface energy of a crystal in a vacuum is calculated from the electrostatic forces between the ions.

J. R. P.

**Anisotropic Liquids. I.** M. BORN (*Sitzungsber. Preuss. Akad. Wiss., Berlin*, 1916, 614—650).—The theory that the molecules of anisotropic liquids are elongated in the direction of one axis, and that the orientations between the axes depend on the temperature, according to a law of distribution, is completed by the calculation of the law of distribution, on the assumption that the molecules are electrical dipoles, and that the directive forces are purely electrical. The liquid crystal is then analogous to the magnet considered in the theory of Langevin and Weiss. The Curie point of a magnet corresponds approximately with the transition point between anisotropic and isotropic states. From the known transition points of anisotropic liquids, the electric moments of the dipoles are calculated. The optical properties of the substances are also calculated, and found in qualitative agreement with experiment. A liquid composed of dipoles will exhibit double refraction in an electric field at sufficiently high temperatures; the expression for Kerr's constant deduced on this theory is similar to that found by Langevin in another manner.

J. R. P.

**Anisotropic Liquids. II. Dependence of the Refractive Index at Right Angles to the Optic-axis on the Temperature.** M. BORN and F. STUMPF (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1916, 1043—1060).—Measurements of the change of refractive

index with temperature made with anisotropic liquids confirm the theory advanced by one of the authors (see previous abstract).

J. R. P.

### **An Altered Formulation of the Quantum Hypothesis.** M.

PLANCK (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1914, 918—923).—The expression for the energy of a resonator derived from the quantum hypothesis may be obtained on the assumptions that: (1) the exchange of energy between resonators and radiation is continuous, instead of quantum emission and continuous absorption postulated in a previous hypothesis; (2) exchange of energy between resonators and free particles (molecules, ions, and electrons) occurs in quanta. The formulæ of the classical electrodynamics then apply to the reciprocal action between resonators and radiation, and many former difficulties are removed. In the collision of a free particle with a resonator, it is assumed that the latter gives up the whole of its energy to the particle, whilst the particle imparts to the resonator amounts of energy which are whole multiples of the quantum. The free particles in solids may be vapour molecules, since the number required is so small as not to contribute materially to the specific heat of the solid. J. R. P.

**Variance and the means of Presuming its Value without the Aid of any Formula.** C. RAVEAU (*Compt. rend.*, 1920, 170, 1385—1387).—A theoretical discussion of the variance of systems, certain systems being discussed and their variance arrived at without calculation. W. G.

**Equilibrium between Chlorine, Water, Hydrochloric Acid, and Chloric Acid. Free Energy of the Chlorate Ion.** AXEL R. OLSON (*J. Amer. Chem. Soc.*, 1920, 42, 896—904).—The equilibrium constant of the reaction  $3\text{H}_2\text{O} + 3\text{Cl}_2 = \text{HClO}_3 + 5\text{HCl}$  has been experimentally determined at  $91^\circ$ . The reaction mixture was sealed in glass tubes with a little (0.02*M*) manganous chloride, which acted as a catalyst. Equilibrium was slowly reached from both sides, and by means of the equation

$$K' = (\text{H}')^6 \times (\text{Cl}')^5 \times (\text{ClO}_3') / (\text{Cl}_2)^3$$

the equilibrium constant is calculated to  $10 \times 10^{-6}$ . The free energy of the reaction  $3\text{Cl}_2(\text{aq.}) + 3\text{H}_2\text{O}(\text{liq.}) = 6\text{H}' + 5\text{Cl}' + \text{ClO}_3'$  is 10,600 cal. at  $91^\circ$ , and at  $15^\circ$  it is 6640 cal. The free energy of formation of the chlorate ion is given from the equation  $0.5\text{Cl}_2(\text{gas}) + 1.5\text{O}_2 + \ominus = \text{ClO}_3'$ , for which  $\Delta F_{298} = -1374$ .

J. F. S.

**Registration of Rapid Pressure Changes.** W. NERNST (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1915, 896—901).—The behaviour of vibrating membranes used in pressure measurements during gaseous explosions is considered mathematically. The rise of pressure during explosion in a closed vessel is stated to follow the law,  $p = p_0(1 - e^{-at})$ , where  $p_0$  is the maximum pressure,  $t$  is the time, and  $a$  is a constant. The main results, however, are

independent of this special hypothesis. Of the two solutions of the equation, only one has been realised with gaseous explosions, namely, the execution by the registering membrane of vibrations of small amplitude about the position corresponding with the instantaneous pressure. The other solution may be represented by high explosives of the "brisant" type. Great disturbances in the motion of the membrane may occur when wave motion is set up in the gas.

J. R. P.

### **The Use of Conductometric Titrations in Neutralisation Analysis. I. The Neutralisation of Acids and Bases.**

I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, **111**, 1—27).—The object of the experiments was to investigate the relationship between the neutralisation curve on the one hand and the dissociation constants and dilution on the other. The experiments were conducted by titrating a dilute acid solution with a relatively strong solution of the base, so that the dilution of the liquid of which the conductivity was being determined was not appreciably changed during the titration. The neutralisation curve was obtained by plotting the relative conductivities as ordinates against the quantities of alkali added as abscissæ. When a strong acid is neutralised by a strong base, the neutralisation curve falls steeply as a straight line to the neutral point, and then rises steeply as the alkalinity increases. Up to the neutral point, the neutralisation curve is the resultant sum of the acid conductivity curve and the salt conductivity curve. By titrating a solution of the salt into pure water, a curve is obtained, the salt conductivity curve, which cuts the neutralisation curve at the neutral point. The sharpness of the neutral point is independent of the mobility of the anion, but the point becomes less distinct on the neutralisation curve the greater the mobility of the cation.

When an acid of medium strength, such as salicylic acid, is neutralised by a strong base, the neutralisation curve has a concave form and passes through a minimum before the neutral point is reached. Beyond the neutral point, the curve rises sharply as a straight line, but the neutral point is not distinct. It can, however, be found by determining the conductivity curve of the salt, since the salt curve cuts the neutralisation curve in the neutral point. The conductivity of the unneutralised acid at any stage of the neutralisation can be deduced from the neutralisation curve and the salt conductivity curve, or it can be calculated from the ion mobilities. From the "acid depression curve" so obtained, the dissociation constant of the acid can be calculated. To obtain good titration results at dilutions 0.1, 0.01, 0.001*N*, the dissociation constant of the acid should be less than  $5 \times 10^{-4}$ ,  $5 \times 10^{-5}$ , or  $5 \times 10^{-6}$  respectively.

In the titration of a very weak acid with a strong base, the neutralisation curve may, from the start, correspond practically with the salt curve up to the neutral point; if the acid is very weak and the salt highly hydrolysed, it is impossible to determine the neutral point. The dissociation constant of the acid must be

not less than  $10^{-10}$  for a  $0.1N$ -solution or  $10^{-9}$  for a  $0.01N$ -solution to obtain good results. Boric acid ( $K=6.6 \times 10^{-10}$ ) and phenol ( $K=10^{-10}$ ) were successfully titrated with sodium hydroxide. Weak acids and weak bases can be titrated if their dissociation constants are greater than  $3 \times 10^{-6}$ . Thus acetic acid can be titrated with ammonia, but boric acid cannot, because, on account of the hydrolysis of the neutral salt, the whole neutralisation curve is rounded off, and there is no sharp change of direction at the neutral point.

E. H. R.

**The Use of Conductometric Titrations in Neutralisation Analysis. II. The Simultaneous Titration of Different Acids or Bases.** I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, 111, 28—51. Compare preceding abstract).—When a strong and a weak acid are titrated together, the acid conductivity curve falls at first along a straight line. If, when the stronger acid is nearly neutralised, the conductivity of the weaker acid is not negligible, the point of neutralisation of the strong acid is not sharp on the neutralisation curve. It can, however, be found by plotting the conductivity curve of the salt of the strong acid, and finding the point of intersection of this straight line with the first, straight portion of the neutralisation curve. In this way, hydrochloric acid can be titrated, for example, in presence of formic acid. The point of neutralisation of the formic acid is given sharply by the change of direction of the curve when the solution becomes alkaline. To get good results, when titrating  $0.1N$ -solutions of the two acids in equal concentrations, the dissociation constant of the weaker acid should be less than  $4 \times 10^{-4}$ . Addition of alcohol, which tends to suppress the dissociation of the weak acid, is sometimes advantageous.

Two weak acids can be titrated together in equal concentrations when the ratio of their dissociation constants is smaller than 0.001, but if the concentration of the weaker acid is ten times that of the stronger, the ratio must be smaller than 0.0001. Since, however, the sharpness of the result depends on the magnitude of the angle of intersection of the two straight lines representing the two portions of the neutralisation curve, and the change of direction of the curve depends on the relative mobilities of the anions of the two acids, it follows that the accuracy of the result depends on the mobilities of the anions, and if these are approximately equal, no definite result can be obtained. Thus oxalic acid and tartaric acid, or oxalic acid and phenol, can be titrated together, but not acetic acid and phenol. When a dibasic acid is titrated, the first and second equivalent points can only be found if the two dissociation constants are markedly different. This occurs in the case of oxalic acid. In the case of tartaric acid, the first equivalent point is not sharp even in presence of alcohol, and in the case of succinic acid it cannot be determined at all.

Two weak acids with approximately equal dissociation constants cannot be titrated together, but if the dissociation constants and ion mobilities are known, the composition can be calculated from

the conductivity of the mixture. A fresh determination of the dissociation constant of formic acid gave  $2.05 \times 10^{-4}$  at  $18^{\circ}$ .

The same considerations apply to the titration of mixtures of bases as to mixtures of acids. E. H. R.

**Catalysis of Oxy-hydrogen Gas by Palladium Mixed Crystals.** G. TAMMANN (*Zeitsch. anorg. Chem.*, 1920, **111**, 90—96).—Experiments were made with palladium-silver and palladium-gold alloys, containing from 0 to 100% silver and gold respectively, to determine the influence of the composition of the metal on the temperature at which catalysis of a hydrogen-oxygen mixture (prepared by electrolysis of sodium hydroxide solution) commences and, on cooling, ceases. The observed temperature at which catalysis ceases is generally considerably lower than that at which it commences, because, during cooling, the heat of reaction tends to keep the temperature of the contact surface between catalyst and gas above that of the surroundings. The form of the catalyst also influences the limiting temperatures; for these experiments, the metal was in the form of thin wire wound into a close spiral. With pure palladium, catalysis started at  $145$ — $163^{\circ}$  and ceased at  $35$ — $50^{\circ}$ . In the palladium-silver series, both limiting temperatures rose slowly until the proportion of silver reached 80%, when there was a sudden rise to  $370$ — $380^{\circ}$  (starting temperature) and  $270$ — $276^{\circ}$  (cessation of catalysis). In the palladium-gold series, there was little change up to 70% gold, then a rapid rise of the limiting temperatures over the range from 70% to 100% gold. There appears to be a close connexion between the velocity of solution of hydrogen in the catalyst and the rate of catalysis. In the palladium-silver series between  $200^{\circ}$  and  $300^{\circ}$ , the solubility of hydrogen is very slight in the alloy containing 70—80% silver, and the same is true of the 80% gold alloy in the palladium-gold series. These compositions correspond with the rapid rise observed in the limiting temperature of catalysis. The rate of catalysis probably depends, however, not so much on the actual solubility of hydrogen as on its rate of solution in the catalyst. E. H. R.

**Acceleration of the Decomposition of Hydrogen Peroxide by Colloidal Rhodium.** C. ZENGHELIS and B. PAPACONSTANTINOS (*Compt. rend.*, 1920, **170**, 1178—1180. Compare this vol., ii, 380).—The decomposition of hydrogen peroxide by a colloidal solution of rhodium is a unimolecular reaction, the velocity of which is considerably accelerated by previously bubbling either hydrogen or carbon monoxide through the colloidal solution.

W. G.

**Catalytic Actions at Solid Surfaces. III. Hydrogenation of Acetaldehyde and the Dehydrogenation of Ethyl Alcohol in the Presence of Finely Divided Metals.** E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1920, [A], **97**, 259—264. Compare A., 1919, ii, 403; this vol., ii, 102).—The hydrogenation of acetaldehyde and the dehydrogenation of ethyl alcohol in the presence of metallic nickel and copper have been investigated at

temperatures 120—300°. It is shown that acetaldehyde is converted into ethyl alcohol by hydrogen under these conditions, in the case of copper at 200° the yield of alcohol being 87.6%; in the case of nickel, the aldehyde has a tendency to break up into carbon monoxide and methane. In the dehydrogenation of alcohol in the presence of copper, a yield of 90—95% of acetaldehyde may be obtained at 295—300°. In the dehydrogenation of alcohol, the presence of water improves the yield of acetaldehyde relatively to that of hydrogen. There are always small quantities of by-products, notably *n*-butaldehyde, crotonaldehyde, and ethyl acetate, the total amount of which is normally 1—2%. The presence of a small proportion of water protects acetaldehyde from hydrogenation, and in some cases prevents the action entirely. The primary action of the catalyst in all these cases is to effect an association with the carbon compound, the resulting unstable complex then being resolved into other compounds. J. F. S.

**Catalytic Actions at Solid Surfaces. IV. Interaction of Carbon Monoxide and Steam as Conditioned by Iron Oxide and by Copper.** E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1920, [A], **97**, 265—273. Compare preceding abstract).

—The reaction  $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 + 10,200 \text{ cal.}$  has been studied, using both ferric oxide and copper as contact substances. The reaction has been carried out using 95% carbon monoxide and using water-gas containing 40% carbon monoxide at temperatures from 227° to 600°. It is shown that copper is much less complete in its action than iron oxide at the higher temperatures, but over the range 200—300° it is definitely more active than iron oxide. Copper commences to act at a reasonable rate at about 220°, whereas iron oxide is barely active at 250°, and does not reach full activity until about 400°. On passing water-gas (5.1% carbon dioxide, 39.9% carbon monoxide, and 47.3% hydrogen) with steam in the presence of ammonia through a tube at 350°, sufficient ammonium formate was obtained for purposes of identification. The relative activities of copper and iron oxide toward carbon monoxide and steam at the lower ranges of temperature are closely parallel to their respective powers of decomposing formic acid and steam. The amount of action effected by the copper catalyst declines somewhat after 350°, and the maximum change effected appears to be greater the higher the proportion of carbon monoxide in the gas. J. F. S.

**Heat of Dissociation of Hydrogen according to the Bohr-Debye Atom Model.** M. PLANCK (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 914—931).—The heat of dissociation of a hydrogen molecule is, at sufficiently low temperatures, equal to the difference between the energy of the two atoms and that of the molecule. On the first assumption, that in all the atoms and all the molecules of hydrogen the electrons describe circular orbits with single quanta, the heat of dissociation is found to be 62,100 cal. The actual value is higher, probably in the region of

100,000 cal. On the second assumption, that in all the atoms and all the molecules those electronic orbits which possess less than one quantum are correspondingly probable, the heat of dissociation is found by classical mechanics to be infinite; on the theory of relativity it would be 570,000 cal., which is certainly too high. The value 140,000 cal., in much better agreement, is obtained on the assumption that, in addition to circular orbits, the electrons may perform pendulum oscillations. It is concluded that the arbitrary assumption of circular orbits made by Bohr is not justified.

J. R. P.

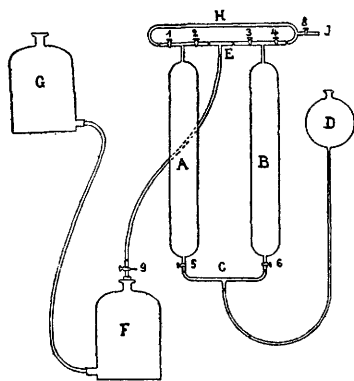
**The Absolute Calculation of Crystal Properties from Bohr's Model Atom.** M. BORN and A. LANDÉ (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1918, 1048—1068).—A mathematical paper in which the positions of the atoms in a cubic space-lattice are deduced from Bohr's model of the atom.

J. R., P.

**Metals. I. and II.** F. HABER (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 506—518, 990—1007).—I. The elastic properties and photoelectric effect are discussed on the hypothesis that a metal consists of a space-lattice of positive ions and free electrons. II. The energies of salts, heats of hydration of ions, the Volta effect, etc., are calculated.

J. R. P.

**Apparatus for Measuring [and Circulating] Gases Soluble in Water.** BERNHARD NEUMANN and HEINRICH SCHNEIDER (*Zeitsch. angew. Chem.*, 1920, **33**, 128).—An apparatus suitable for measuring and circulating small quantities of gas, soluble in water, consists essentially of two pipette-shaped glass vessels, *A* and *B*, provided at the upper ends with T-pieces having stop-cocks, 1, 2, 3, 4, and terminating below in stop-cocks, 5, 6, the latter being connected by a T-piece, *C*, and in communication with a levelling vessel, *D*. The top T-pieces are connected by another T-piece, *E*, as well as by a bent tube, *H*, with a lateral branch, *J*, provided with a stopcock, 8, and leading to the gas reaction vessel or other apparatus. *E* is connected by tubing to a gas collector, *F*, with a three-way tap, 9, and *G* is a pressure vessel for controlling the movement of gas in *F*.



*A* and *B* are first half filled with water saturated with the gas. By suitable manipulation of the stopcocks, gas is introduced into *A*, and the air is expelled through *B*, after which gas is introduced into *B*, the whole apparatus now being filled with gas, and further solution by the

water being prevented. The gas may be circulated through both vessels or retained in either for measurement under atmospheric pressure.

W. J. W.

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## Inorganic Chemistry.

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**Improved Kipp's Apparatus for the Preparation of Chemically Pure Hydrogen in the Laboratory.** M. DOLCH (*Chem. Zeit.*, 1920, **44**, 378).—The gas delivery tube from the central bulb of a Kipp's apparatus is connected by a three-way cock and side-tube to a stopper and three-way cock in the mouth of the top globe, which is also connected through a second tube to a mercury trap. Pure stick zinc is used in the central bulb, and the apparatus is filled with pure hydrogen before the introduction of air-free dilute sulphuric acid. The space above the acid in the top bulb, being connected to the generator bulb, is always filled with hydrogen, which can be drawn off at will from either bulb by suitably placing the three-way cocks. Excess of pressure is released through the mercury trap. E. H. R.

**Triatomic Hydrogen.** GERALD L. WENDT and ROBERT S. LANDAUER (*J. Amer. Chem. Soc.*, 1920, **42**, 930—945).—A reactive modification of hydrogen has been produced by several methods, all of which are dependent on gaseous ionisation: (i) by the  $\alpha$ -rays from radium emanation, (ii) by an electrical discharge under reduced pressure, and (iii) by the high potential corona at atmospheric pressure. Attempts to produce activation by Schumann light rays failed. This active hydrogen reduces sulphur, arsenic, phosphorus, mercury, nitrogen, and both acid and alkaline solutions of potassium permanganate. It is condensed or destroyed by temperatures about that of liquid air. It is very unstable, and reverts to the ordinary form in about a minute. It passes readily through glass wool, and is not less stable at atmospheric pressure than at low pressures. The activity is not due to gaseous ions, and the properties of the gas are quite different from those of Langmuir's atomic hydrogen (A., 1912, ii, 826, 1162; 1914, ii, 104; 1915, ii, 249). The formation of a polyatomic molecule is indicated by the contraction of the hydrogen when ionised. Positive ray analysis at very low pressures shows a large proportion of triatomic molecules, which are undoubtedly the molecules responsible for the chemical activity. All the properties of the gas point to it being an ozone form, perhaps, properly called "*hyzone*." The existence of triatomic hydrogen is applied to the explanation of Lind's "cluster ion" hypothesis (A., 1912, ii, 513). The calculations of Bohr, based on the Rutherford atom, furnish the only valency hypothesis which satisfactorily accounts for the existence of triatomic hydrogen. J. F. S.

**Chemical Decomposition of Hydrogen Peroxide.** CHR. WINTHER (*Danske Vid. Selsk. Math. Phys. Medd.*, 1920, **2**, No. 1, 1—18; from *Chem. Zentr.*, 1920, i, 723).—The author confirms Kistiakowsky's observation that the decomposition of hydrogen peroxide in light is notably catalysed by the presence of potassium ferrocyanide. When dilute mixed solutions are placed in ultra-violet light, decomposition ensues very slowly at first, subsequently more rapidly, and finally attains a constant rate; the phenomenon is explained by the assumption of the gradual formation of an extremely stable substance which catalytically accelerates the decomposition of hydrogen peroxide. H. W.

**The Behaviour of Non-metallic Hydrides towards Chlorine.** ALFRED STOCK [with ROBERT WINTGEN] (*Ber.*, 1920, **53**, [B], 837—842).—The experiments recorded in the literature of this subject are concerned for the most part with the products obtained by rather drastic action. The author gives an extended review of the available data, and describes a series of experiments, some of them of a preliminary nature, on the regulated action of the halogen, the experiments being performed at low temperature and frequently in the presence of an inert solvent, such as liquid hydrogen chloride. In spite of certain gaps in the evidence, the following statements may be made. Only five non-metals yield partly chlorinated hydrides which are stable at the ordinary temperature,  $B_2H_5Cl$ ,  $CH_3Cl$ ,  $SiH_3Cl$ ,  $CH_2Cl_2$ ,  $SiH_2Cl_2$ ,  $CHCl_3$ ,  $SiHCl_3$ ,  $NH_2Cl$ , ( $NHCl_2$  ?),  $OHCl$ . Amongst these, the compounds of boron, nitrogen, and oxygen are most unstable, whilst chloromonosilane is more readily decomposed than methyl chloride, a close dependence on the position of the element in the periodic system being observable. The maximum stability is observed with carbon, and is attributable to the equality in the affinity of this element for positive and negative groups. The stability of the partly chlorinated hydrides diminishes in all directions from carbon. The compounds exhibit a more or less strongly marked tendency to decompose into the pure hydride and pure chloride (for example,  $B_2H_5Cl$  into  $B_2H_6$  and  $BCl_3$ ). In the nitrogen group ( $N, P, As, Sb$ ), in which the instability of the partly chlorinated hydride increases with increasing atomic weight of the nuclear element, reaction immediately occurs, either with the initial hydride or by further action of the initial decomposition products among themselves, whereby hydrogen chloride is eliminated, and either condensed hydrides relatively poorer in hydrogen ( $N_2H_4, P_2H_4$ ; that is,  $NH_2Cl + NH_3 = N_2H_4 + HCl$ ) or the free elements (that is,  $AsCl_3 + AsH_3 = 2As + 3HCl$ ) are formed. The former frequently are further converted into solid hydrides still poorer in hydrogen ( $P_{12}H_6, P_8H_2, AsH[?]$ ). In the oxygen group, the ability to form a partly chlorinated hydride is only observed in the element of smallest atomic weight, oxygen itself ( $OHCl$ ). In this compound, the tendency towards decomposition into hydride and chloride is still observable ( $2OHCl = OH_2 + OCl_2$ ), but the change to hydrogen

chloride and oxygen is more characteristic. Correspondingly, the action of chlorine on the remaining hydrides of the oxygen group leads exclusively to the formation of the free elements, S, Se, Te.

H. W.

**Electrolysis of Hydrogen Bromide in Liquid Sulphur Dioxide.** LANCELOT SALISBURY BAGSTER and GEORGE COOLING (T., 1920, 117, 693—696).

**Bromine Chloride: its Combination with Ethylene.** MARCEL DELÉPINE and LUCIEN VILLE (*Compt. rend.*, 1920, 170, 1390—1392).—Although physical chemists deny the existence of a bromine chloride, the authors consider that the behaviour of a solution of chlorine in bromine towards ethylene, the main product being chlorobromoethane, is strong evidence in favour of the existence of such a compound.

W. G.

**The Photochemical Oxidation of Hydrogen Iodide.** CHR. WINTHER (*Danske Vid. Selsk. Math. Phys. Medd.*, 1920, 2, No. 2, 1—28; from *Chem. Zentr.*, 1920, i, 723—724).—Thin, rapidly moved layers of hydrogen iodide solution, when subjected to the conjoint action of oxygen at a constant pressure and light, are oxidised very slowly initially, then more rapidly until the process attains a constant velocity. The phenomenon is due to the auto-sensitising action of the liberated iodine. Similar action is observed in the cases of the photochemical oxidation of the leuco-bases of certain dyes (Gros, 1901), of alkaline solutions of pyrogallol (Trautz and Thomas, 1908), and of aqueous sodium sulphite solution (Trautz, 1909). In each instance, a slow oxidation at any rate must be assumed to occur in the dark.

H. W.

**The Estimation of the Density of Oxygen according to Dewar and Kamerlingh Onnes.** RUDOLF MEWES (*Zeitsch. Sauerstoff Stickstoff Ind.*, 1920, 12, 14; from *Chem. Zentr.*, 1920, i, 664).—The data obtained by Dewar in 1902 and by Onnes in 1911 for the vapour density of oxygen are in good agreement at  $-182^{\circ}$  with Gay-Lussac's law, although the latter is known not to hold at such low temperatures. The author now shows that the values for the apparent alteration in volume are in accordance with the law, but that such values are not in reality the data which are to be determined; after applying the necessary corrections, much lower results are obtained.

H. W.

**Rutherford's Experiments on the Subdivision of the Nitrogen Nucleus.** W. LENZ (*Naturwiss.*, 1920, 8, 181—186; from *Chem. Zentr.*, 1920, i, 768).—The theory of relativity, according to which mass is connected with every energy, throws light on the questions of simple numbers for atomic weights and of the stability of nuclei. From this point of view, the stability of the helium nucleus is readily understood, whilst the instability of the nitrogen nucleus is explicable. The author considers the persistent oxygen radiations to be possibly helium  $\alpha$ -rays.

H. W.

**Action of Nitrous Acid on Coloured Indicators.** C. MATIGNON and G. GIRE (*Bull. Soc. chim.*, 1920, [iv], **27**, 362—366).—A mixture of nitric and nitrous acids was titrated with *N*/10-sodium hydroxide, different indicators being used for the different titrations. Of the indicators used, only sodium ferric salicylate characterised the nitrous acid, and this was not sharp. Thus nitrous acid, contrary to the conclusions derived from the heats of neutralisation, is a much stronger acid than the second acid function of phosphoric acid. This is borne out by a study, by electrical conductivity measurements, of the progressive displacement of nitrous acid by sulphuric acid in a dilute solution of sodium nitrite.

W. G.

**Production of Concentrated Nitric Acid from Nitrous Gases.** F. FOERSTER, TH. BURCHARDT, and E. FRICKE (*Zeitsch. angew. Chem.*, 1920, **33**, 113—117, 122—127, 129—132).—The concentration of nitric acid above 68—69%, by treatment of dilute nitric acid with nitrogen peroxide, water, and oxygen, may be effected if the time of treatment is extended, the oxygen used only in slight excess, and the gas velocity reduced. Even so, only 80% nitric acid is produced. A very high concentration results by interaction of the weak nitric acid solution with sufficient excess of liquid nitrogen peroxide, followed by slight agitation with oxygen. When the equilibrium  $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$  is reached in the treatment of nitrous gases with water, nitric peroxide dissolves, and thereby initiates the interaction  $\text{N}_2\text{O}_4 + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_3 + \text{HNO}_2$ , the nitrous acid being then decomposed into nitric acid and nitric oxide, and oxidised.

W. J. W.

**Red Phosphorus as a Reducing Agent.** LUDWIG ROSENSTEIN (*J. Amer. Chem. Soc.*, 1920, **42**, 883—888).—The reactions between red phosphorus and acid solutions of a number of salts have been investigated, and a possible application of this substance as a reagent in qualitative analysis has been indicated. The experiments were effected by boiling the solution with 200 mg. of red phosphorus for a few minutes. Silver salts yield an insoluble phosphide, mercuric and mercurous salts are reduced to the metal, palladium and osmium salts are reduced either to the metal or a phosphide, gold salts are converted into an insoluble phosphide, stannic salts are partly reduced to stannous salts, ferric salts are reduced to ferrous salts, iridic salts to iridous, selenates are reduced to the element or to an insoluble phosphide, molybdates are reduced to quadrivalent molybdenum salts, vanadates are reduced to tervalent vanadium salts, dichromates to chromic salts, and permanganates to manganous salts. Bismuth, lead, cadmium, antimony, and arsenic salts, arsenates and stannous salts, are not reduced by red phosphorus. Tellurates and platinichlorides are reduced very slowly by red phosphorus.

J. F. S.

**Carbon Formed in the Reaction between Calcium Carbide and Nitrogen.** A. REMELÉ and B. RASSOW (*Zeitsch. angew. Chem.*, 1920, **33**, 139—140).—On decomposing calcium cyanamide

(obtained by the interaction of calcium carbide and nitrogen) with water at 160—180° to produce ammonia, the products of the decomposition included small quantities of carbon. This was freed from the bulk of calcium carbonate by treatment with hydrochloric acid, and was purified by fusion with potassium hydroxide or treatment with hydrofluoric acid. It was thus left as graphitic carbon containing 98.15 to 99.4% C, 0.13 to 1.64% H, and 0.43 to 1.48% of residue. It had  $D^{15.5}_D$  2.250, ignited at 600—640°, and closely resembled Acheson graphite in its electrical conductivity. When oxidised, it yielded a graphitic acid containing 54.81% C, 1.79% H, and 43.40% O, and showing only very slight colloidal properties. When fused with potassium hydroxide, it reacted (like Acheson graphite) at 500°, with the evolution of hydrogen, whereas Ceylon graphite yielded scarcely any gas at 750°. It was not attacked by strong nitric acid.

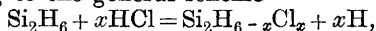
C. A. M.

**Charcoal before the War. II.** WILDER D. BANCROFT (*J. Physical Chem.*, 1920, **24**, 201—224. Compare this vol., ii, 309).—A general discussion on charcoal, in which the removal of inorganic matter, such as calcium carbonate and calcium sulphate, from charcoal which has been used in sugar refining is discussed. The decolorising power of bone-black and methods of preparing synthetic bone-black are considered.

J. F. S.

**Silicon Hydrides. VIII. Halogen Derivatives of Disilane and their Hydrolysis.** ALFRED STOCK and KARL SOMIESKI (*Ber.*, 1920, **53**, [B], 759—769. Compare A., 1916, ii, 319; 1918, ii, 110, 111; this vol., ii, 31).—The behaviour of disilane,  $\text{Si}_2\text{H}_6$ , towards halogen acids has been investigated, and is found to resemble closely that of monosilane.

Disilane does not appear to react with hydrogen chloride at the ordinary temperature or at 120°; in the presence of a little sublimed aluminium chloride, however, reaction occurs more or less readily, according to the general scheme



and the course can be followed readily by condensation, by liquid air, of all the components, except hydrogen, and measurement of the volume of the latter. The activity of the aluminium chloride appears to vary considerably with different preparations, and a satisfactory explanation of this behaviour is not at present forthcoming. A mixture of chlorides is invariably produced, the equilibrium lying in favour of the intermediate members of the series. Thus with hydrogen chloride (1 vol.) and disilane (less than 1 vol.), the main product is *dichlorodisilane*, very little *monochlorodisilane* being obtained; with the gases in the volume ratio 2:1, much *trichlorodisilane*, in addition to *dichlorodisilane*, is produced. Complete chlorination is not, however, effected by a large excess of hydrogen chloride. By reason of the small amount produced, it has not been found possible to isolate *monochlorodisilane* in the pure state. The final purification of *dichlorodisilane* could also

not be effected, since it forms a mixture of constant boiling point with trichlorodisilane. The experiments, however, indicate that, as in the case of the carbon compounds, mixtures of isomerides are formed in the halogenation of disilane.

The bromination of disilane has been studied in a precisely analogous manner, and *monobromodisilane*, m. p.  $-100^{\circ}$  to  $-101^{\circ}$ , has been isolated in a state of purity. As in the case of the chlorination, the tendency towards the formation of higher derivatives is very pronounced; for instance, in the action of equal volumes of hydrogen bromide and disilane, less than one-third of that portion of the latter which undergoes reaction is converted into the monobromo-derivative.

The hydrolysis of the halogenated disilanes corresponds exactly with that of the similar monosilanes. Thus monobromodisilane readily reacts with water to yield the *substance*,  $(\text{Si}_2\text{H}_5)_2\text{O}$ , colourless liquid, which can be volatilised without decomposition, and, when dissolved in benzene, instantaneously reduces cold silver nitrate, but not copper sulphate, solution. It reacts slowly but quantitatively with sodium hydroxide solution in accordance with the equation  $(\text{Si}_2\text{H}_5)_2\text{O} + 8\text{NaOH} + 3\text{H}_2\text{O} = 4\text{Na}_2\text{SiO}_3 + 12\text{H}_2$ . The solid products obtained by the hydrolysis of dibromodisilane and more highly halogenated derivatives closely resemble silico-oxalic acid,  $(\text{HO}_2\text{Si}\cdot\text{SiO}_2\text{H})_x$ . They are only slowly hydrolysed further by water, can be dried in a desiccator without marked decomposition, are blackened by silver nitrate solution, owing to the deposition of metallic silver, evolve hydrogen when treated with alkali hydroxide, and finally yield a residue of silicate, and explode feebly when heated on platinum foil, evolving gas and becoming discoloured. Evidently the Si-Si linking remains intact in them. This bond appears to be more stable towards alkali than would be expected from earlier statements. Thus two stages can be clearly distinguished in the action of alkali on  $(\text{Si}_2\text{H}_4\text{O})_x$ , namely, a violent evolution of gas with accompanying solution of the substance, and then a much slower, persistent change, which can speedily be brought to an end by warming the solution. The first phase corresponds with the hydrolytic separation of the hydrogen atoms,  $(\text{Si}_2\text{H}_4\text{O})_x + 3\text{H}_2\text{O} = (\text{HO}_2\text{Si}\cdot\text{SiO}_2\text{H})_x + 4\text{H}_2\text{O}$ , whilst the second is due to the gradual conversion of sodium silico-oxalate into sodium silicate and hydrogen.

H. W.

**Prolonged Action of Carbonic Acid on Silicates and Quartz.** C. MATIGNON and (Mlle) MARCHAL (*Compt. rend.*, 1920, 170, 1184—1186).—Quartz, wollastonite, diopase, mica, talc, asbestos, and glass, respectively, in aqueous suspension were submitted to the action of carbon dioxide under 10 atmos. pressure for ten years and three months. At the end of this time, all the silicates and the quartz itself were more or less corroded, and varying amounts of silica had passed into solution. Wollastonite showed the greatest signs of attack and the glass the least.

W. G.

**Action of Alcohol on the Sulphates of Sodium.** GERALD SNOWDEN BUTLER and HORACE BARRATT DUNNICLIFF (T., 1920, 117, 649—667).

**Search for an Alkali Element of Higher Atomic Weight than Cæsium.** L. M. DENNIS and R. W. G. WYCKOFF (*J. Amer. Chem. Soc.*, 1920, 42, 985—990).—The alkalis from 3500 grams of pollucite, which contains more than 30% of cæsium oxide, have been examined to see if they contain the next higher homologue of cæsium. The mineral was decomposed by boiling with hydrochloric acid, and, after dilution, filtered. The filtrate was treated with ammonia and ammonium carbonate, whereby a precipitate, consisting mainly of aluminium hydroxide, was obtained. To guard against possible loss of ekacæsium at this point, the aluminium hydroxide was dissolved in sulphuric acid, and the alums thus formed were recrystallised until the ammonium alum had been eliminated. The residual alums were added to those obtained later and treated as described below.

The filtrate from the aluminium hydroxide was evaporated and the residue converted into chlorides, of which 1250 grams were obtained. These were submitted to a series of fractional crystallisations and precipitations with hydrogen chloride. The most soluble fraction, which, according to the order of the solubilities of the alkali chlorides, would contain ekacæsium chloride, was converted into perchlorates, which were fractionally dissolved until the least soluble fraction had been reduced to 10 grams. The end fractions all showed the presence of cæsium alone, and no fraction indicated the presence of ekacæsium when the arc spectrum was examined. The majority of the chlorides were converted into sulphates and fractionated until only 200 c.c. of the saturated solution remained; this, on examination by the arc spectrum, contained only cæsium. The last fraction of the sulphate crystallisation was converted into the alums, and these fractionated, but in no fraction was there any indication of ekacæsium. [See also Richards and Archibald, A., 1903, ii, 366; Baxter, A., 1915, ii, 97.] J. F. S.

**Melting Point of Normal Ammonium Sulphate.** CARL CASPAR (*Ber.*, 1920, 53, [B], 821).—When heated in an open tube, normal ammonium sulphate softens at about 310°, melts at 336—339°, and decomposes, with evolution of gas, at 355°; in a closed tube it softens from about 360°, and has m. p. 417—423°. The datum, 140°, recorded in the literature is based on a misapprehension, and refers in reality to ammonium hydrogen sulphate. H. W.

**Solubility of Mono- and Di-ammonium Phosphate.** G. H. BUCHANAN and G. B. WINNER (*J. Ind. Eng. Chem.*, 1920, 12, 448—451).—The solubility (grams in 100 grams of the saturated solution) of monoammonium phosphate between 5° and 90° is  $18.0 + 0.455t$ ; that of diammonium phosphate between 10° and 70° is  $36.5 + 0.213t$ . W. P. S.

**Mixed Colloids of Calcium Fluoride.** A. MAZZUCHELLI and D. VITA (*Gazzetta*, 1920, **50**, i, 232—245. See Paternò and Mazzucchelli, A., 1904, ii, 169).—Colloidal calcium fluoride, prepared by pouring potassium fluoride solution into excess of calcium chloride solution, possesses a negative charge, this observation being in accord with the behaviour noted by Lottermoser with silver salts, which in the colloidal state exhibit the sign of the ion in excess at the moment of their formation (A., 1905, ii, 586). Mixed colloidal solutions containing calcium fluoride and another insoluble salt have been prepared by mixing solutions of suitable salts. Moderately stable mixed colloidal solutions are formed by calcium fluoride with  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$ ,  $\text{Ag}_3\text{PO}_4$ ,  $\text{Ag}_2\text{S}$ ,  $\text{CuS}$ ,  $\text{Fe}(\text{OH})_3$ , and  $\text{Si}(\text{OH})_4$ , the last of these being thus obtained in the colloidal condition in a solution neutral to methyl-orange. Less stable colloidal solutions, obtainable only under certain conditions, are formed with  $\text{CaCO}_3$ ,  $\text{CaC}_2\text{O}_4$ ,  $\text{AgCNS}$ ,  $\text{Ag}_2\text{CrO}_4$ ,  $\text{Ag}_2\text{MoO}_4$ ,  $\text{ZnS}$ ,  $\text{CdS}$ ,  $\text{MnS}$ ,  $\text{PbCrO}_4$ ,  $\text{PbSO}_4$  (very slightly stable), and  $\text{BaSO}_4$ . With  $\text{As}_2\text{S}_3$ , immediate precipitation occurs.

T. H. P.

**Slaked Lime and Milk of Lime.** BERNHARD KOSMANN (*Zeitsch. Elektrochem.*, 1920, **26**, 173—181).—Polemical: a long discussion on the processes occurring in the slaking of lime, in which the views of Kohlschütter and Walther (A., 1919, ii, 342) are criticised. The author is of the opinion that the slaking of lime consists in a gradual step-wise combination with water, in which the following substances are produced in order:  $\text{Ca}(\text{OH})_2$ ,  $\text{HCa}(\text{OH})_3$ ,  $\text{H}_2\text{Ca}(\text{OH})_4$ ,  $\text{H}_3\text{Ca}(\text{OH})_5$ ,  $\text{H}_4\text{Ca}(\text{OH})_6$ ,  $\text{H}_5\text{Ca}(\text{OH})_7$ ,  $\text{H}_6\text{Ca}(\text{OH})_8$ , and  $\text{H}_7\text{Ca}(\text{OH})_9$ .

J. F. S.

[**Slaked Lime and Milk of Lime.**] V. KOHLSCHÜTTER (*Zeitsch. Elektrochem.*, 1920, **26**, 181—182).—An answer to Kosmann (preceding abstract).

J. F. S.

**An Unusual Deposit of Aragonite from Sea Water.** ROGER C. WELLS (*J. Washington Acad. Sci.*, 1920, **10**, 249—254).—Small crystals of aragonite were found on the walls of a sealed glass tube which had contained sea-water for several years. The most probable explanation of the formation of the deposit is that alkali had been slowly dissolved from the glass, causing partial conversion of calcium hydrogen carbonate into carbonate. The solubility product  $[\text{Ca}^{++}][\text{CO}_3^{--}]$  for the sea-water under consideration is calculated to be  $7.2 \times 10^{-10}$  at  $25^\circ$ .

E. H. R.

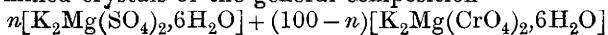
**Reactions between Primary Potassium Phosphate and Increasing Quantities of Calcium Hydrogen Carbonate during Boiling.** W. WINDISCH and W. DIETRICH (*Woch. Brau.*, 1920, **37**, 177—180, 187—189).—The precipitates obtained by boiling solutions of primary potassium phosphate with increasing proportions of calcium hydrogen carbonate show increasing percentages of calcium, which range from that corresponding with



secondary to that corresponding with tertiary calcium phosphate. The precipitates appear to entrain soluble alkaline compounds, since the alkalinities of the filtrates (due to formation of secondary potassium phosphate) are lower than the calculated values.

L. E.

**A Sulphato-chromate Regarded as an Individual Substance.** A. DUFFOUR (*Bull. Soc. franç. Min.*, 1919, **42**, 247; from *Chem. Zentr.*, 1920, i, 726).—The author has vainly endeavoured to repeat the preparation of potassium magnesium sulphato-chromate,  $2\text{MgSO}_4 \cdot \text{K}_2\text{CrO}_4 \cdot 9\text{H}_2\text{O}$ , described by Etard (this Journ., 1877, ii, 847). Crystals similar to those obtained by the latter separate from a solution containing magnesium sulphate (2 mols.) and potassium chromate (1 mol.), but these are assigned by the crystallographical properties to the series of isomorphous magnesium double sulphates, which they also resemble chemically in losing two-thirds of their water of crystallisation at  $120^\circ$ . A case of mixed crystals of the general composition



is obviously presented; in the present instance,  $n = 84.5$ , whereas with Etard's preparation, the analyses of which were confined to the estimation of  $\text{CrO}_3$  and of the loss at  $250^\circ$ , the value of  $n$  was 64.5. The loss in weight at  $250^\circ$ , however, exceeds the weight of water, since magnesium chromate begins to decompose, with evolution of oxygen, at this temperature. From a solution of a molar mixture of sulphate and chromate, the former separates first isomorphously mixed with 5.5 mols.% of the latter; after separation of the excess of potassium salts, the first mixed crystals of potassium magnesium sulphato-chromate have  $n = 72.4$ . From solutions richer in chromate, for example, from such as contain three times as much double chromate as double sulphate, the double salt immediately separates in triclinic crystals ( $+ 2\text{H}_2\text{O}$ ). When, however, the solution is allowed to evaporate at  $20^\circ$ , with careful exclusion of any seed of the triclinic salt, a monoclinic *hexahydrate* may be obtained in small amount, the composition of which approximates to that of the mother liquor. The compound is, however, metastable, and, after a few days, shows efflorescent patches of the triclinic dihydrate, into which it is slowly transformed.

H. W.

**Crystalline Structure of Zinc Oxide.** W. LAWRENCE BRAGG (*Phil. Mag.*, 1920, [vi], **39**, 647—651).—The crystalline structure of zinc oxide has been determined by measurement of the X-ray spectrum. It is shown that the zinc atoms are arranged on two hexagonal space-lattices, their centres corresponding very closely with those of a set of equal spheres in hexagonal close packing. In the latter case, the axial ratio is  $a:c = 1:1.632$ , whilst that for zinc oxide is  $a:c = 1:1.608$ . The positions of the zinc atoms are identical with those of the hexagonal close-packed arrangement of spheres, if the latter be supposed to contract in the direction parallel to the hexagonal axis, so as to reduce the ratio  $c/a$  from

1.632 to 1.608. The oxygen atoms are probably on two hexagonal space-lattices identical with those on which the zinc atoms are situated, and derived from the latter by a movement of translation parallel to the  $c$  axis, which brings every oxygen atom into the centre of four zinc atoms arranged at the corners of what is very nearly a regular tetrahedron. The observed spacings agree well with the calculated values; they are: plane (0001),  $c/2 = 2.58$  Å.U.; (1010),  $a\sqrt{3}/2 = 2.80$  Å.U.; (1120),  $a/2 = 1.61$  Å.U.; (1011), 2.47 Å.U.  
J. F. S.

**Atomic Weight of Lead from a Japanese Radioactive Mineral.** THEODORE W. RICHARDS and JITSUSABURO SAMESHIMA (*J. Amer. Chem. Soc.*, 1920, **42**, 928—930).—Lead obtained from a mineral crust found at the bottom of a hot spring in Hokuto, Formosa, Japan, has been used for atomic weight determinations. This mineral, according to Hayakawa and Nakano (*A.*, 1912, ii, 1123), contains also cerium, barium, lanthanum, ionium, polonium, and radium, but no uranium or radio-lead. The metallic lead was converted into the chloride, and the ratio  $\text{PbCl}_2 : 2\text{Ag}$  determined by Richards's method (*A.*, 1914, ii, 653), when, as the mean of three determinations, the value 207.13 was obtained for the atomic weight. This indicates that the material is mainly ordinary lead, with possibly 5% of an isotope of lower atomic weight.  
J. F. S.

### The Separation of the Rare Earths by Basic Precipitation.

**I. WILHELM PRANDTL and JOHANNA RAUCHENBERGER** (*Ber.*, 1920, **53**, [B], 843—853).—In its usual form the basic process for the separation of the rare earths suffers from the drawback that the solubility of the precipitated hydroxides or basic salts in the mother liquor is, in general, very small, and the absolute difference in solubility between the hydroxides of neighbouring earths is minimal; in order, therefore, to avoid local excesses of hydroxyl ions and to achieve a reasonably successful fractionation, it is necessary to work with exceedingly dilute solutions which necessitate lengthy evaporations, etc. An amended process is now proposed which permits the use of solutions of any concentration, it being only necessary to ensure that precipitation is sufficiently slow to be truly selective, and that the most sparingly soluble substance actually separates. This can be effected more advantageously by increasing the solubility of the precipitate in the mother liquor than by simple dilution, whilst at the same time the absolute differences in solubility between the precipitates of neighbouring earths is increased and their precipitation is delayed. Since the reaction between ammonia and the salts of the alkaline earths is reversible,  $\text{MCl}_2 + 3\text{NH}_4\cdot\text{OH} \rightleftharpoons \text{M}(\text{OH})_2 + 3\text{NH}_4\text{Cl}$ , its course is dependent on the concentration of the ammonium salt; increase in the concentration of the latter increases the solubility of the earth hydroxide in the mother liquor within certain limits, and delays its precipitation by ammonia.

The authors have attempted to measure the equilibrium of the reaction under varying conditions in the cases of lanthanum, neodymium, and praseodymium, and have obtained similar, but not identical, results by approaching the subject from the two sides. Since it is found that the precipitate does not consist of the pure hydroxide, but of a strongly basic chloride of varying composition, the pure oxides were treated at the requisite temperature with ammonium chloride solution on the one hand and the basic chlorides so formed were subjected to the action of 1, 2, 3, 4, and 5*N*-ammonium chloride solution, whilst, on the other hand, the metallic chlorides were treated with the equivalent quantity of ammonia and so much ammonium chloride as to make 1, 2, 3, 4, and 5*N*-solutions of the latter at 15°, 30°, 50°, and 100° in closed vessels until equilibrium was established, after which the amount of ammonia and of earth in the solution were estimated. It is found that the solubility of the basic salts (formed from the oxides) in ammonium chloride solution is always less than that of the basic salts obtained by precipitation with ammonia. In either case, the solubility of the precipitates increases to a maximum with 3*N*-ammonium chloride solution, and then diminishes. It is also observed that under otherwise similar conditions, the content of the solution in earthy metal, but not that of ammonia, to a marked extent depends on the amount of the precipitate, which indicates an adsorption of the (partly colloiddally) dissolved earthy salt by the precipitate. The curves also show that lanthanum is relatively greatly distinguished from the didymium component by its greater basicity, and that neodymium and praseodymium are very similar in this respect. They also indicate an extremely important influence of temperature on the separation process; the lanthanum curves for 2 and 3*N*-ammonium chloride solution are so widely separated from the didymium curves at 50° that a separation should be readily possible, whilst, on the other hand, at a slightly higher temperature, but still under 100°, the curves intersect, so that a separation is then impossible. The praseodymium and neodymium curves generally lie very close together and intersect at definite temperatures. The approximation of the curves at higher temperatures is probably explained by the more complete conversion of the precipitate into the hydroxides, the absolute differences between the solubilities of which are very slight.

Basing their procedure on the experiments just detailed, the authors describe a very successful method for the separation of lanthanum from its mixtures with much didymium. The impure oxide is dissolved to a nearly neutral solution in moderately concentrated hydrochloric acid, an amount of ammonium chloride equal to the weight of the oxide is added, and sufficient water to make the solution 2—3*N* with respect to ammonium chloride. The solution is heated to 50° in a capacious porcelain dish, and a mixture of equal volumes of 4*N*-ammonia and 4*N*-ammonium chloride solutions is slowly added with vigorous stirring. As soon as a moderate amount of precipitate has been formed (about 5% of the

original oxide) the operation is interrupted, the precipitate is removed, and a second precipitation is effected in the clear filtrate. The alternate precipitation and filtration are repeated in this manner until the filtrate no longer exhibits absorption lines.

H. W.

### **The Action of Concentrated Sulphuric Acid on Iron. III.**

CHARLES E. FAWSITT (*J. Soc. Chem. Ind.*, 1920, **39**, 147—148T. Compare A., 1914, ii, 274).—Experiments on the effect of concentrated sulphuric acid of different strengths on a steel containing C, 0.51%; P, 0.046%; Si, 0.083%; S, 0.058%; and Mn, 0.48%, showed that the velocity of attack increased as the acid was diluted from 97% to 90.9%  $\text{H}_2\text{SO}_4$ ; it appeared then to drop suddenly at 89.3%, and below 85% increased rapidly. Shaking has an important effect in increasing the velocity of action. Steel which has been made passive by immersion in nitric acid will sometimes resist the action of concentrated sulphuric acid, but at times the treatment fails to afford protection. In some instances partial immersion of a piece of steel in nitric acid has caused the whole piece to resist the action of sulphuric acid. The addition of nitric acid or a nitrate to the sulphuric acid, however, intensifies its action on steel. The effect of the addition of a number of substances to the sulphuric acid was investigated, including potassium persulphate, sodium sulphate, sodium hyposulphite, and arsenious acid, but none of these had any appreciable protective action.

E. H. R.

### **The Nickel Plating of Aluminium and its Alloys.**

LÉON GUILLET and MAXIME GASNIER (*Compt. rend.*, 1920, **170**, 1253—1256).—The surface of the aluminium is first prepared by subjecting it to a sand blast. The sand should be capable of passing through a 0.2 mm. sieve, and be used under a pressure of 1500 grams/cm.<sup>2</sup> The nickel deposit should not be thicker than 0.01 mm. If a thicker deposit is required it is preferable to apply first a thin deposit of nickel, then a deposit of copper 0.02 mm. thick, and then a further deposit of nickel. [See, further, *J. Soc. Chem. Ind.*, 1920, 492A.]

W. G.

### **Revision of the Atomic Weight of Tin. Electrolytic Estimation of Tin in Tin Tetrachloride.**

GREGORY PAUL BAXTER and HOWARD WARNER STARKWEATHER (*J. Amer. Chem. Soc.*, 1920, **42**, 905—917).—The atomic weight of tin has been determined from estimations of tin in stannic chloride. Stannic chloride prepared from very pure electrolytic tin was subjected to a careful fractional distillation, and portions were decomposed under 0.3*N*-hydrochloric acid, and the solution thus obtained electrolysed, using a mercury cathode which was weighed. The metal obtained from the stannic chloride was shown by means of its spectrum to contain less than 0.001% of lead and copper. Two series of experiments were carried out, the first of which gives a mean of 118.700 for the atomic weight, whilst the second series gives 118.707. The mean value of the atomic weight is therefore 118.703 from sixteen experiments. (Cl=35.457.)

J. F. S.

**Revision of the Atomic Weight of Tin. I.** BOHUSLAV BRAUNER and HENRY KREPELKA (*J. Amer. Chem. Soc.*, 1920, **42**, 917—925).—The atomic weight of tin has been determined by the analysis of tin tetrabromide by means of silver, and the ratio  $\text{SnBr}_4 : 4\text{Ag}$  obtained; four experiments were carried out, three of which are in good agreement, and yield a mean value of 118.70 for the atomic weight ( $\text{Br} = 79.916$ ). The fourth experiment is discarded because of an impurity in the silver nitrate used. Other methods are investigated, (i) the oxidation of tin with nitric acid; this method is useless because of absorbed products in the metastannic acid formed; it yields 118.02, which increases to 118.66 when the stannic oxide is fused with potassium hydrogen sulphate. The electrolysis of diammonium stannic chloride gives a value 119.03, which is too high because of difficulties in the complete reduction of the cathode deposit after heating. The synthesis of stannic bromide was found to be unworkable on account of the difficulty in estimating the excess of bromine in the stannic bromide.

J. F. S.

**Revision of the Atomic Weight of Tin. II.** HENRY KREPELKA (*J. Amer. Chem. Soc.*, 1920, **42**, 925—928. Compare preceding abstract).—A further series of atomic-weight determinations for tin. The method was a determination of the ratio  $\text{SnBr}_4 : 4\text{Ag}$ . Greater precautions were taken to exclude moisture from the stannic bromide. The mean value of the ratio  $\text{SnBr}_4 : 4\text{Ag}$  is found from six experiments to be 1.01586, the extreme values being 1.01580 and 1.01592. From this the atomic weight  $118.699 \pm 0.016$  is calculated.

J. F. S.

**A New Series of Complex Compounds: Antimonyoxyiodides.** A. C. VOURNAZOS (*Compt. rend.*, 1920, **170**, 1256—1259).—When antimony tri-iodide is decomposed by water to give antimony oxyiodide there is an indication of the intermediate formation of an unstable complex acid,  $\text{H}_2(\text{SbOI}_3)$ . In support of this view it has been possible to prepare the corresponding mercury and copper salts. When antimony tri-iodide and mercuric cyanide in equimolecular proportions are warmed in moist amyl alcohol on a water-bath for four to six hours *mercury antimonyoxyiodide*,  $\text{Hg}(\text{SbOI}_3)$ , m. p.  $78^\circ$ , is obtained. This compound is decomposed by concentrated acids, but can be recrystallised from cold dilute hydrochloric acid. It is decomposed by alkali hydroxides. With copper acetate under similar conditions antimony tri-iodide gives *copper antimonyoxyiodide*,  $\text{Cu}(\text{SbOI}_3)$ .

If mercury cyanide and antimony tri-iodide are heated together in dry xylene, *mercury antimonyiodocyanide*,  $\text{Hg}[\text{SbI}_3(\text{CN})_2]$ , is obtained, which, when treated with moist amyl alcohol, gives the antimonyoxyiodide described above. If the heating in xylene is continued, a *trimercury antimonyiodocyanide*,  $\text{Hg}_3[\text{Sb}_2\text{I}_6(\text{CN})_6]$ , is obtained. Under similar conditions, cuprous cyanide yields *cuprous antimonyiodocyanide*,  $\text{Cu}_6[\text{Sb}_2\text{I}_6(\text{CN})_6]$ .

W. G.

**The Mathematical Possibility of Increasing the Yield or of Reducing the Proportion of the Reacting Substances in certain Chemical Reactions. II.** ANGEL PÉREZ HERNÁNDEZ (*Anal. Soc. Quim. Argentina*, 1918, **6**, 306—322).—The author's method (this vol., ii, 107) is further illustrated by application to the equation  $\text{Sb}_2\text{S}_3 + 8\text{KNO}_3 + 3\text{C}_2 = \text{Sb}_2 + 3\text{K}_2\text{SO}_4 + \text{K}_2\text{CO}_3 + 4\text{CO}_2 + \text{CO} + 4\text{N}_2$ .  
W. R. S.

**The Properties of Mixtures of Selenium and Antimony.** H. PÉLABON (*Ann. Chim.*, 1920, [ix], **13**, 121—153).—A microscopic examination of mixtures of selenium and antimony fused together shows that, for certain proportions of the constituents, the liquid mixture may be formed of two phases, the densities of which are nearly equal, and that the only compound that can be obtained in the pure state by direct fusion of the two elements is the selenide,  $\text{Sb}_2\text{Se}_3$ . A study of the *E.M.F.* of solution of these alloys shows that it increases at first with the time, and finally tends towards a constant value. This value will vary with the relative proportions of antimony and selenium present, and if the *E.M.F.*'s are plotted against the antimony content there is a sharp inflexion corresponding with the selenide  $\text{Sb}_2\text{Se}_3$ . All alloys richer in antimony than the selenide  $\text{Sb}_2\text{Se}_3$  give piles sensitive to light, the *E.M.F.* rising sharply on illumination and then dropping slowly, the drop becoming sharp when the source of light is removed. The red rays are the most active in promoting this effect.

With a pile in open circuit the *E.M.F.* diminishes gradually with rise in temperature, but in closed circuit the *E.M.F.* increases rapidly as the temperature rises.

Curves are given showing the variations in the resistance and thermoelectric power of mixtures of antimony and selenium with variations in composition and temperature.  
W. G.

**Bibliography of the Metals of the Platinum Group. Platinum, Palladium, Iridium, Rhodium, Osmium, Ruthenium, 1748–1917.** JAS. L. HOWE and H. C. HOLTZ (*U.S. Geol. Survey, Bull.*, 1919, **694**, 454 pp.).

CHEMICAL ABSTRACTS.

### Mineralogical Chemistry.

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**The Oxidation of the Ingredients of Banded Bituminous Coal. Composition of Coal.** FREDERICK VINCENT TIDESWELL and RICHARD VERNON WHEELER (T., 1920, **117**, 794—801).

**Analysis of a Pyrargyrite.** CARLOS CASTRO (*Bol. Min. Mexico*, 1919, **7**, 275—277).—The pyrargyrite analysed came from Union de Providencia, San Felipe, State of Guanajuato, Mexico. The

crystals were separated from matrix and pulverised, and the sulphide mineral was decomposed by heating in a current of chlorine. The mineral consisted of: pyrrargyrite, 98.34; argentite, 1.61; pyrite, 0.37%, of which the pyrrargyrite was represented by: S, 17.40; Sb, 22.13; Ag, 58.81%.

CHEMICAL ABSTRACTS.

### Bäckströmite, an Orthorhombic Modification of $\text{Mn}(\text{OH})_2$ .

G. AMINOFF (*Geol. För. Förh.*, 1919, **41**, 473—491).—Black orthorhombic ( $a:b:c=0.7393:1:0.6918$ ) crystals, occurring with pyrochroite in the calcite veins at the Långban mines, Sweden, are believed to represent a new modification of manganous hydroxide, to which the name *bäckströmite* is given. In composition, however, they are near to manganite, as shown by the following analyses by R. Mauzelius:

	$\text{Mn}_2\text{O}_3$ .	$\text{MnO}$ .	O.	$\text{MgO}$ .	$\text{CaO}$ .	$\text{PbO}$ .
I.....	77.80	11.59	—	1.68	0.14	0.04
II.....	—	—	8.19	2.31		trace

	$\text{Sb}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{H}_2\text{O}$ (+130°).	$\text{H}_2\text{O}$ (-130°).	Total.
I.....	0.07	0.14	5.16	3.24	99.86
II.....	trace	0.43	8.59	3.54	—

Other determinations gave: O (in excess of  $\text{MnO}$ ), 8.15, 8.67;  $\text{H}_2\text{O}$  (+130°), 9.05, 8.57;  $\text{H}_2\text{O}$  (-130°), 3.27, 3.65%. A partial analysis of the associated, altered pyrochroite gave: O, 8.26;  $\text{H}_2\text{O}$  (+130°), 8.31;  $\text{H}_2\text{O}$  (-130°), 3.94%. The crystals are often encrusted with a regular intergrowth of pyrochroite, the rhombohedral modification of manganous hydroxide; and Röntgenograms on the face (010) are identical with those on the face (111) of pyrochroite. It is therefore concluded that the crystals represent double pseudomorphs, the change being *bäckströmite* → *pyrochroite* → *manganite*. Other compounds of the type  $\text{R}''(\text{OH})_2$  belonging to this isodimorphous series are the rhombohedral  $\text{Mg}(\text{OH})_2$  (brucite),  $\text{Ca}(\text{OH})_2$ , and  $\text{Cd}(\text{OH})_2$ , and the orthorhombic  $\text{Ca}(\text{OH})_2$  and  $\text{Zn}(\text{OH})_2$ .

L. J. S.

**Sphenomanganite from Långban, Sweden.** GUST. FLINK (*Geol. För. Förh.*, 1919, **41**, 329—336).—Crystals of manganite, D 4.29, exhibiting a sphenoidal habit, but otherwise identical with ordinary manganite, gave on analysis by Mauzelius:

	$\text{Mn}_2\text{O}_3$ .	$\text{MnO}$ .	O.	$\text{Fe}_2\text{O}_3$ .	$\text{MgO}$ .	$\text{BaO}$ .	$\text{H}_2\text{O}$ .	Total.*
I.....	—	79.60	8.76	0.35	0.87	—	10.16	100.22
II.....	81.1	8.1	—	0.7	0.6	1.6	7.3	99.4

\* Incl.  $\text{SiO}_2$  0.11,  $\text{Sb}_2\text{O}_3$  0.25,  $\text{CaO}$  trace,  $\text{PbO}$  0.10.

CHEMICAL ABSTRACTS (L. J. S.)

**Chubutite and the meaning of its Discovery.** E. RIMANN (*Anal. Soc. Quim. Argentina*, 1918, **6**, 323—328).—The author points out that lead oxide is dimorphous, as it crystallises in the tetragonal and rhombic systems (Larsen, *Amer. Min.*, 1917, **2**, 18), whilst the known oxychlorides of lead crystallise as follows:



penfieldite,  $\text{PbO} \cdot 2\text{PbCl}_2$ , hexagonal; matlockite,  $2\text{PbO} \cdot 2\text{PbCl}_2$ , tetragonal; mendipite,  $4\text{PbO} \cdot 2\text{PbCl}_2$ , rhombic; pseudomendipite,  $6\text{PbO} \cdot 2\text{PbCl}_2$ , rhombic; loretoite,  $13\text{PbO} \cdot 2\text{PbCl}_2$ , and chubutite,  $14\text{PbO} \cdot 2\text{PbCl}_2$ , tetragonal. It is suggested that the oxychlorides of lead form a continuous series, and that the dimorphism of lead oxide persists in the mixed crystals, although the dimorphous modifications of one and the same oxychloride have not yet been observed. The determination of the optical constants and the melting points of the oxychlorides should be helpful towards elucidating the question.

W. R. S.

**Baryto-celestine and the Relation of Anhydrite to Celestine and Barytes.** WERNER GRAHMANN (*Jahrb. Min.*, 1920, 1, 1—23).—To elucidate the isomorphous relationships between anhydrite, celestine, and barytes, the thermal method was applied to determine how the transition point of each substance is affected by admixture with one of the others, whilst density determinations of the mixtures were also made. The transition points of the pure substances are: calcium sulphate,  $1193^\circ$ ; strontium sulphate,  $1152^\circ$ ; barium sulphate,  $1149^\circ$ . For the experiments, the pure sulphates were ground together in the desired proportions and heated in a platinum crucible to a few degrees above the transition point. The cooling curve was then followed by means of a platinum-platinum-rhodium couple. The condition diagrams for the three binary systems are given. Strontium and barium sulphates are miscible in all proportions in both  $\alpha$ - and  $\beta$ -forms, and baryto-celestine is therefore a true isomorphous mixture. Calcium and strontium sulphates are completely miscible in the  $\alpha$ -form above the transition temperature, but in the  $\beta$ -form they are isodimorphous. Addition of strontium sulphate to calcium sulphate first raises the transition temperature up to about 20 mols. %  $\text{SrSO}_4$ ; then up to 80 mols. % the transition temperature gradually falls to a minimum at  $1010^\circ$ . The saturated  $\beta$ -mixed crystals co-existing at the eutectic temperature contain 55 to 82 mols. %  $\text{SrSO}_4$ . The density curves indicate that the form of strontium sulphate isomorphous with anhydrite should have a density of 3.55, whilst the second form of calcium sulphate should have a density of 3.29. Barium sulphate and calcium sulphate are likewise isodimorphous, and their miscibility is slight, at most 5 mols. % of calcium sulphate in the barium sulphate crystals. The compositions of naturally occurring minerals are in full agreement with the experimental results, and it is suggested that the name baryto-celestine should be confined to minerals containing between 10 and 90 mols. % of barium or strontium sulphate.

E. H. R.

**Aluminium Sulphate from Chile.** ATILIO A. BADO (*Bol. Minero Soc. Nac. Min. (Chile)*, 1919, 31, 196—197).—A white, fibrous mineral, referred to keramohalite, gave:

$\text{Al}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	$\text{SO}_3$ .	$\text{H}_2\text{O}$ .
17.76	0.05	trace	0.39	37.38	44.77

A small part (0.367%) of the sulphuric acid is free. According to *Anal. Soc. Cient. Argentina*, **73**, 351, this analysis corresponds with 54.70%  $\text{Al}_2(\text{SO}_4)_3$ , and the formula is  $\text{Al}_2\text{O}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . This appears to be identical with the basic sulphate investigated by Marguerite (*Compt. rend.*, 1880, **90**, 1354). The mineral forms rhombohedral crystals, and is readily soluble in water. It undergoes hydrolysis in dilute solution, and is capable of coagulating suspended matters.

CHEMICAL ABSTRACTS (L. J. S.).

**A New Mineral from Katanga.** G. CESÀRO (*Ann. Soc. Géol. Belgique*, 1912, **39**, Bull. 241; Annexe to vol. 39, *Publ. relatives au Congo Belge*, 41—48).—Crusts of minute, blue or greenish-blue crystals are found on limestone and sandstone in the Étoile du Congo copper mine. The crystals are orthorhombic, with  $a:b:c=0.9844:1.07679$  or  $0.9771:1.07872$ ;  $H\ 5\frac{1}{2}$ ,  $n$  about 1.7, birefringence about 0.120,  $2E\ 55^\circ$ , optically negative. Qualitative tests show it to be a copper cobalt phosphate, and from the similarity of the crystallographic and optical properties to those of libethenite, olivenite, etc., the formula is probably  $(\text{Cu},\text{Co})(\text{OH})\text{PO}_4$ .

For this mineral the name *cornetite* has been proposed by H. Buttgenbach (*Les Minéraux et les Roches, Liège*, 1916).

CHEMICAL ABSTRACTS. (L. J. S.)

**Amblygonite from Utö.** HELGE BACKLUND (*Geol. Foren. Förh.*, 1918, **40**, 757—775).—The mineral had  $D\ 3.065$ ,  $\alpha\ 1.5910$ ,  $\beta\ 1.6046$ ,  $\gamma\ 1.6125$ ,  $2V$  about  $80^\circ$ ,  $p > v$ . The analysis by Sahlbom gave:

$\text{SiO}_2$ .	$\text{P}_2\text{O}_5$ .	$\text{Al}_2\text{O}_3$ .	$\text{Na}_2\text{O}$ .	$\text{Li}_2\text{O}$ .	F.	$\text{H}_2\text{O}$ .	Total.
3.50	43.40	33.54	2.71	7.84	11.10	2.18	104.27

CHEMICAL ABSTRACTS.

**Meta-torbernite I, its Physical Properties and Relation to Torbernite.** A. F. HALLIMOND (*Min. Mag.*, 1920, **19**, 43—47).—"Torbernite" from Gunnislake, Cornwall, suffered no loss in weight over 55% sulphuric acid at the ordinary temperature, but over concentrated acid it slowly lost water, amounting to 10.1% after more than a year. This material is really meta-torbernite I (A., 1916, ii, 258), differing from the torbernite hitherto examined (which has  $D\ 3.22$ ; refractive indices,  $\omega\ 1.592$ ,  $\epsilon\ 1.582$ ; axial ratio,  $a:c=1:2.97$ ). This natural meta-torbernite I has  $D\ 3.683$ ,  $3.700$ ,  $\omega\ 1.623$ ,  $\epsilon\ 1.625$  (N. L. Bowen, 1919), and  $a:c=1:2.28$ . When torbernite,  $D\ 3.219$ , is converted into meta-torbernite I by heating under water for several hours at  $100^\circ$ , the density changes to 3.67, and there is a loss in weight of 7.11%, corresponding with the change from  $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}$  to  $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ . The first formula represents torbernite and the latter meta-torbernite I. A morphotropic relation exists between the crystals of the two substances, and the extra four molecules of water are held in layers that alternate with basal layers having the con-

stitution of meta-torbernite I. From the molecular volumes, it is calculated that this extra water has a density of 1.2 in the crystal.

L. J. S.

**Pyrobelonite, a New Lead-Manganese Vanadate from Långban, Sweden.** GUST. FLINK (*Geol. För. Förh.*, 1919, **41**, 433—447).—This new mineral forms deep-red crystals with adamantine to sub-metallic lustre, which are orthorhombic ( $a:b:c=0.8040:1:0.6509$ ) with prismatic or acicular habit. It is brittle, without cleavage; H  $3\frac{1}{2}$ , D 5.377. Associated minerals are hausmannite, barytes, barysilite, pyrochroite, etc. Analyses by Mauzelius gave (Mn:Pb=7:4):

	V <sub>2</sub> O <sub>5</sub> .	P <sub>2</sub> O <sub>5</sub> .	PbO.	FeO.	MnO.	MgO.	CaO.	H <sub>2</sub> O.	SiO <sub>2</sub> .
I.....	19.81	0.05	48.99	0.51	25.03	0.66	0.62	n.d.	0.22
II.....	20.26	—	48.74	0.48	24.99	0.53	0.92	n.d.	0.22

The crystallographic and optical characters show a relation to those of descloizite.

CHEMICAL ABSTRACTS (L. J. S.).

**Gearksutite at Gingin, Western Australia.** EDWARD S. SIMPSON (*Min. Mag.*, 1920, **19**, 23—39).—This rare mineral, previously known only in granite-pegmatite at three localities, has been found as small nodules embedded in Cretaceous greensand at Gingin, forty miles north of Perth. It is white, earthy, and very friable. Under the microscope, it shows minute, angular particles, which are birefringent and have refractive index about 1.445. D 2.710—2.720. Associated minerals are phosphatic nodules, glauconite, kaolinite, halloysite, calcite, limonite, quartz grains, and some organic matter; gibbsite  $[\text{Al}(\text{OH})_3]$  is also found in an underlying shale. Analysis I is of the greensand matrix freed from any visible gearksutite. II, by H. BOWLEY, of a dark grey, phosphatic nodule consisting of fluorapatite (57.7%) with calcite (11.4%) and included glauconite, quartz (15%), microcline, and organic matter. III of fossil wood petrified by apatite from greensand at Dandarragan (fifty miles north of Gingin), where it is associated with dufrenite and some vivianite and wavellite. IV, by H. BOWLEY, of gearksutite.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	K <sub>2</sub> O.
I.....	59.79	8.15	10.47	0.33	nil	2.96	2.32	2.84
II.....	17.83	2.24	2.26	—	—	40.60	1.00	1.10
III.....	1.26	trace	1.01	—	0.78	53.88	1.17	—

	Na <sub>2</sub> O.	H <sub>2</sub> O.	H <sub>2</sub> O.	CO <sub>2</sub> .	P <sub>2</sub> O <sub>5</sub> .	F.	Organic.	Total less O for F.
I.....	0.17	5.17	4.73	0.25	1.72	0.77	0.42	99.86*
II.....	0.66	0.04	2.11	5.02	24.80	2.94	0.48	99.84
III.....	—	0.22	0.80	1.31	38.80	3.00	0.18	101.16†

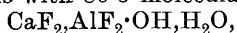
	Al.	Ca.	K.	Na.	F.	H <sub>2</sub> O.	H <sub>2</sub> O.	O.	Total.
IV.....	15.38	22.13	0.06	0.06	41.26	0.12	15.88	[4.88]	100.00†

\* Incl. TiO<sub>2</sub> 0.09.

† Incl. Cl 0.01.

† Incl. Fe<sub>2</sub>O<sub>3</sub>, 0.03; K<sub>2</sub>O, 0.01, present as glauconite; quartz, 0.19; P<sub>2</sub>O<sub>5</sub>, trace.

Gearsutite is readily soluble in cold dilute acids, and the solution etches glass. It is decomposed by a hot dilute solution of sodium hydroxide. No water is lost below  $270^{\circ}$ , and less than one-fifth at  $300^{\circ}$ ; at  $320^{\circ}$  the loss is 14.00%. Heated rapidly to a red heat, it gives off hydrofluoric acid in addition to water. Analysis IV corresponds with 86.5 molecular % of



with 13.5 molecular % of  $\text{CaF}_2, \text{AlF}(\text{OH})_2, \text{H}_2\text{O}$ . The genesis of the mineral is discussed and equations given. In granite-pegmatite it is of pneumatolytic origin; hydrogen fluoride acting on the feldspars of the rock gives, in the first place, normal anhydrous salts (cryolite, etc.), and later, with the cooling of the solution, normal hydrous salts (pachnolite and thomsenolite), and, lastly, basic salts (gearsutite, topaz, etc.). In the sedimentary rock at Gingin, the mineral has evidently been produced by the action of carbonated water on fluorapatite and gibbsite.

L. J. S.

**Meteoric Iron from Yenberrie, Northern Territory of Australia.** JOHN C. H. MINGAYE (*J. Washington Acad. Sci.*, 1920, 10, 314—316).—A mass weighing about 291 lb. was found in 1918 embedded in sandy soil about twenty miles S.S.E. of Yenberrie. The structure is that of a coarse octahedrite with very thin plates of taenite. Anal. I is of the metallic portion, D 7.304. Duplicate determinations gave Ni + Co 7.46, P 0.195, C 0.065. In 100 grams of the iron 0.00026 gram of platinum was found. Tin and gold could not be detected. II is of a black, brittle material found coating pieces of metal from a dark nodule in the centre of the mass. This consists mainly of sulphide and phosphide. III of small, brown plates and laths, extremely brittle and strongly magnetic. It consists largely of schreibersite with magnetite and carbon.

	Fe.	Ni.	Co.	Cu.	P.	S.	C.
I.....	92.35	5.98	1.43	0.017	0.161	trace	0.073
II.....	65.38	6.10	0.37	trace	4.14	13.06	4.94
III.....	73.22	6.35	0.25	0.02	5.02	nil.	2.51
	Cl.	SiO <sub>2</sub> .	Ca.	Mg.	O.	Total.	
I.....	0.003	0.140	—	—	—	100.154	
II.....	0.08	—	0.23	nil	5.70	100.00	
III.....	n.d.	0.28	0.20	0.07	12.08	100.00	

L. J. S.

**Rhythmic Tubular Rust Formation in Meteoric Iron from Cañon Diablo.** K. ENDELL (*Kolloid. Zeitsch.*, 1920, 26, 215—217).—In specimens of meteoric iron, rust (ferric oxide and hydroxide) is found, which penetrates into the iron mass in the form of a tube which exhibits a rhythmic structure. The formation is held to be due to the setting up of local electric currents when the mass is moist, whereby ferrous hydroxide is first formed; this is oxidised, and the ferric hydroxide is deposited. J. F. S.

## Analytical Chemistry.

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**Theory of Gravimetric Analysis, with Special Reference to Sources of Error.** L. MOSER (*Zeitsch. anal. Chem.*, 1920, **59**, 1—10).—A discussion on the accuracy of general gravimetric methods. Errors which cannot be eliminated completely are those due to solubility of precipitates, induced precipitation, formation of solid solutions, and adsorption, occlusion, and inclusion. Other sources of error, more under control, are those due to the action of atmospheric oxygen or carbon dioxide on the precipitate, contamination from glass vessels, and decrepitation or partial volatilisation during ignition. The different errors may have a compensating effect. W. P. S.

**Yellow Light in Polarimetric Determinations.** LUIS GUGLIALMELLI (*Anal. Soc. Quim. Argentina*, 1918, **6**, 497—499).—To obviate the drawbacks of the use of sodium chloride, Dupont (A., 1897, ii, 77) proposed a mixture of salt and trisodium phosphate; this is found to work very satisfactorily. For its preparation, 1 gram-molecule of disodium phosphate is dissolved in water and treated with 1 gram-molecule each of sodium hydroxide and chloride. The solution is evaporated to dryness and the residue fused. W. R. S.

**Colorimetric Estimations with Solutions containing Two Coloured Substances.** K. GEORGE FALK and HELEN MILLER NOYES (*J. Biol. Chem.*, 1920, **42**, 109—130).—The authors have examined with much care the principles underlying the ordinary use of the colorimeter for quantitative work, particularly in such cases as the Benedict method for the estimation of dextrose, where two coloured substances are present. From this study, it is shown that there is grave danger of the introduction of serious errors in such methods unless the standard and the unknown solutions are nearly alike in composition and concentration. J. C. D.

**A Photographic Turbidimeter.** W. G. BOWERS and JACOB MOYER (*J. Biol. Chem.*, 1920, **42**, 191—198).—The apparatus, which is described and illustrated, is fashioned so that a strong light is passed through a definite and comparatively narrow column of the substance in question, and what is not lost falls on one side of an oil spot on paper. On the other side of the spot falls a beam of light of equal initial intensity, in the path of which standardised ground glass disks are inserted until equality of illumination is obtained. J. C. D.

**Decomposition (or Removal) of Ammonium Sulphide in Qualitative Analysis.** F. FEIGL (*Zeitsch. anal. Chem.*, 1920, **59**, 12—15).—When a solution containing ammonium sulphide is warmed with the addition of a slight excess of lead hydroxide and filtered, a clear filtrate is obtained which is free from lead and

sulphur. This method is preferable to the usual procedure for removing excess of ammonium sulphide (acidifying and boiling to expel hydrogen sulphide), since colloidal sulphur is not formed and there is no danger of oxidising a portion of the sulphur, with the formation of sulphuric acid, which would interfere with subsequent tests for alkali earths.

W. P. S.

**Estimation of Bromine.** F. WÜNSCHE (*Arch. exp. Path. Pharm.*, 1919, **84**, 328—339).—In order to estimate bromine in organic matter, the substance is dried with sodium peroxide in a nickel basin, first on a water-bath, then on a free flame, and eventually incinerated. The ash is extracted with distilled water and filtered, and the filtrate neutralised with concentrated sulphuric acid and treated with potassium permanganate and sulphuric acid. The free bromine is carried over by means of a current of air into a vessel containing a known volume of magenta and sulphurous acid. The bromine is then estimated colorimetrically by comparing the violet coloration which is produced with a set of standards. Two mg. of neuronal were estimated in 30 c.c. of blood with an error of 12%. Neuronal, adaline, and bromural were estimated in frog's tissue by this method with an error of about 7%.

S. S. Z.

**Kendall's Method of Estimating Iodine in Thyroid Preparations.** S. B. KUZIRIAN (*Proc. Iowa Acad. Sci.*, 1918, **25**, 495—496).—(1) In destroying organic matter, it is advantageous to use more sodium hydroxide and less potassium nitrate to obviate the formation of large quantities of nitrite, which tend to liberate iodine. (2) Organic substances with high ash content often contain iron or some other interfering element, which ought to be eliminated before trustworthy results can be obtained. Filtration at this point does not altogether eliminate the interfering action of ash. When, however, the sodium hydroxide fusion was taken up with hot water, a few grams of sodium carbonate and some talc added, and the solution brought to boiling and kept boiling for a few minutes, set aside for two hours, and filtered, the filtrate was free from interfering basic elements. (3) In acidifying the above filtrate with 85% syrupy phosphoric acid, the author's experience was well in accord with that of Forbes, Beegle, and others, who found that one or two drops of phosphoric acid in excess was insufficient to assure expulsion of all bromine. Even after the addition of 1.5 to 2 c.c. in excess, the whole of the bromine could be boiled off without causing any loss of iodine. This was shown by taking an aliquot of accurately standardised alcoholic solution of iodoform and estimating iodine according to Kendall's method. No loss of iodine occurred when 2 c.c. of acid were added in excess. (4) In boiling off the bromine, it was made a practice to dilute the filtrate to more than 400 c.c. and boil down to 250 c.c., thus assuring a complete expulsion of bromine. Under these conditions, the author found the method applicable

for tankage, roughage, and other organic substances with a high per cent. of ash.

CHEMICAL ABSTRACTS.

**Modifications in the Technique of Estimating Oxygen in Blood with Van Slyke's Apparatus.** E. P. POULTON (*Proc. Physiol. Soc.*, 1920; *J. Physiol.*, 1920, **53**, lxi. Compare A., 1918, ii, 82).—Modifications have been introduced which avoid certain errors due to the presence of dissolved air in the reagents, and which shorten the estimation. Ten c.c. of dilute ammonia are shaken with some crystals of potassium ferricyanide, a trace of saponin, and four or five drops of octyl alcohol. The mixture is placed in the cup and drawn completely into the apparatus, and sealed with mercury. By reducing the pressure, the dissolved air is withdrawn from the reagent, which is then returned to the cup. The blood pipette has a small ring of fine rubber tubing round the tip. By this means, the pipette, when full of blood, is pressed down beneath the ferricyanide mixture on to the bottom of the cup, and on turning the upper tap of the apparatus, the blood is delivered directly into the burette without admixture with the reagent. On removing the pipette, the last portion of the blood is washed in by the ferricyanide mixture, 2 or 3 c.c. of the latter being allowed to remain behind in the cup. The tap is then sealed with mercury.

J. C. D.

**Detection of Water in Alcohol and other Organic Solvents.** F. HENLE (*Ber.*, 1920, **53**, [B], 719—722).—When normal aluminium ethoxide is heated at about 340° until the temperature, as indicated by an immersed thermometer, begins to fall, it yields a heavy, yellow, semi-solid mass, the composition of which corresponds with the formula  $\text{Al}_2(\text{OEt})_4\text{O}$ ; if the action is continued until the thermometer indicates 330° or less, a brittle, yellow resin is obtained, which has the approximate composition  $\text{Al}_4(\text{OEt})_6\text{O}_3$ . Both substances are soluble in xylene and are suitable for the detection of water, the latter compound being the more sensitive. The reagent may be readily prepared in a single operation by treating aluminium turnings with absolute alcohol and a little mercuric chloride, heating the product for several hours on the water-bath until the aluminium ethoxide appears dry, distilling off the alcohol of crystallisation at 210—220°, and finally heating the crude aluminium ethoxide at about 340° for an hour. The product is dissolved in about a litre of dry xylene and the solution filtered through a dry paper. The clear, pale yellowish-brown filtrate can be preserved indefinitely in the absence of moisture and air. The test is carried out by adding a few drops of the xylene solution to a few c.c. of the liquid under investigation; according to the quantity of water present, a voluminous, gelatinous precipitate of aluminium hydroxide is produced immediately or after a few seconds. Distinct evidence is obtained in the various cases, with the percentage of water enclosed in brackets after the name of the solvent: ethyl alcohol (0.05), methyl alcohol (0.1), ethyl ether (0.005), ethyl acetate (0.1), acet-

aldehyde (0.1), acetone (1). The two substances last named may also yield a white turbidity, due to the precipitation of excess of the ethoxide, which, however, may readily be distinguished from aluminium hydroxide, as it readily dissolves in xylene or in an excess of the reagent. H. W.

### **Oxidation in Relation to the Estimation of Sulphites.**

H. I. WATERMAN (*Chem. Weekblad*, 1920, 17, 196—197).—The oxidation of sulphite solutions in air, as measured by the increasing volume of the solution required to reduce a given quantity of iodine, proceeds fairly rapidly in the case of sodium hydrogen sulphite and very rapidly in the case of normal sodium sulphite, the hydroxyl ions present in the latter being probably catalytically active. Addition of sodium hydroxide accelerates the oxidation. Accurate estimations of sulphite were obtained by dissolving the salt in a boiled 5% glycerol solution in a flask filled with carbon dioxide. A measured quantity of this solution is run into excess of acid standard iodine solution, also under carbon dioxide, and the residual iodine titrated with thiosulphate. W. S. M.

**An All-glass Nitrogen Apparatus.** E. R. ALLEN and B. S. DAVISSON (*Ann. Missouri Bot. Gardens*, 1919, 6, 45—48).—The apparatus is of the usual Kjeldahl form. The advantages claimed are: the elimination of rubber connexions; efficient scrubbing of entrained alkali from the steam; the use of Pyrex glass, which does not yield an appreciable amount of alkali to steam or to boiling solutions. The rigidity may be lessened by one rubber connexion between the distilling bulb and the Kjeldahl flask if the glass ends are kept close together. The distilling bulb has a capacity of 200 c.c.; steam enters it through a re-curved tube with a perforated end. Thus the bulb acts as a trap for scrubbing the steam. CHEMICAL ABSTRACTS.

**1. Modified Kjeldahl Method. 2. Carbazole Test for Nitrites. 3. Colour Test for Tryptophan in Urine.** W. A. FEARON (*Dub. J. Med. Sci.*, 1920, [iv], No. 1, 28—32; from *Physiol. Abstr.*, 1920, 5, 79).—(1) The best proportion of the constituents in the acid mixture for incineration is given. Steam distillation is best, but Cole's method of distilling with alcohol is also good and rapid. Methyl-red is recommended as an indicator. (2) All urines give a colour with sulphuric acid, but the tint varies from orange vermillion to deep violet; a large number of substances might give colours: (a) pigments and chromogens from bile and blood, and (b) from indole and derivatives from intestinal putrefaction which reach the urine via the blood. The red colour is attributed to indole derivatives reacting with the  $\alpha$ -nitro-group. Nitrites give a green colour with carbazole. (3) The usual tests are not adequate to detect tryptophan in urine, because of the presence of other indole compounds. If the urine is treated with an excess of the Hopkins-Cole reagent and a drop of the mixture is added to concentrated sulphuric acid, the tryptophan condensation



product (allied to carbazole) gives a deep green colour with the nitrites of urine. Tryptophan in urine is rare. J. C. D.

**Sensitive Reaction for Nitrites.** P. H. HERMANS (*Pharm. Weekblad*, 1920, **57**, 462—463).—The following gives a sensitive reaction for nitrite in presence of nitrate. To 2 c.c. of the solution to be tested a few drops of glacial acetic acid are added, and then 2 c.c. of 5% potassium oxalate solution, 1 c.c. of 5% manganous sulphate solution, and a few drops of 3% hydrogen peroxide. A red coloration indicates nitrite. 0.02 Gram of sodium nitrite per litre can be detected in this way. W. S. M.

**Detection of Arsenic in Sulphur.** HAROLD S. DAVIS and MARY D. DAVIS (*J. Ind. Eng. Chem.*, 1920, **12**, 479—480).—Schaeppi's method of detecting arsenic in sulphur (extraction with warm ammonia and treatment of the solution with silver nitrate to precipitate the dissolved sulphide) is untrustworthy, since sulphur itself dissolves in ammonia, and the resulting ammonium sulphide gives a precipitate of silver sulphide. The best method consists in oxidising the sulphur with bromine and nitric acid, and applying the Gutzeit test to the residue. W. P. S.

**Iodometric Estimation of Arsenic Acid.** P. FLEURY (*J. Pharm. Chim.*, 1920, [vii], **21**, 385—391).—The reaction  $\text{As}_2\text{O}_5 + 4\text{HI} = \text{As}_2\text{O}_3 + 2\text{I}_2 + 2\text{H}_2\text{O}$  is complete in five minutes when the reacting mixture is heated at  $100^\circ$  and contains 25% of potassium iodide and 3.65% of hydrogen chloride. A quantity of arsenate equivalent to about 50 c.c. of  $N/10$ -iodine solution is dissolved in 30 c.c. of water, 3 c.c. of hydrochloric acid ( $D\ 1.171$ ) are added, and the mixture is heated on a boiling water-bath for five minutes; 25% of potassium iodide is then added, the heating continued for a further five minutes, and, after the mixture has been cooled, the iodine is titrated with  $N/10$ -thiosulphate solution. Owing to the action of dissolved oxygen on hydriodic acid, the amount of iodine is always larger than that which should correspond with the arsenic acid. An excess of sodium hydrogen carbonate is then added to the mixture and the arsenious acid titrated with  $N/10$ -iodine solution. W. P. S.

[**Estimation of Arsenic Acid in Presence of Arsenious Acid.**] GEORG JOACHIMOGLU (*Arch. expt. Path. Pharm.*, 1916, **80**, 8—24).—See this vol., i, 510.

**Spectroscopic Methods for Estimating Carbon Monoxide in Blood.** H. HARTRIDGE (*Proc. Physiol. Soc.*, 1920; *J. Physiol.*, 1920, **53**, lxxvii—lxxviii).—The most satisfactory method was found to be one previously described by the author (*A.*, 1912, ii, 488). J. C. D.

**The Estimation of Carbon Dioxide and Fermentable Sugars.** ARTHUR SLATOR (*J. Soc. Chem. Ind.*, 1920, **39**, 149—151*t*).—The estimation of carbon dioxide is carried out as follows. The

carbonate solution is placed in a distillation flask connected through the neck opening to a trap leading to a condenser and receiver containing standard barium hydroxide solution. To the side-arm of the distillation flask is connected by means of pressure tubing a small tube containing dilute sulphuric acid. The pressure tubing is clipped, while the whole apparatus is being exhausted, the clip then removed, and the acid in the small tube is boiled over into the distillation flask. The solution in the latter is then boiled, and the carbon dioxide absorbed by the barium hydroxide is determined by titration. The apparatus has been used for determining the quantity of carbon dioxide produced during the fermentation of sugars. The fermentation was allowed to proceed in a small tube sealed off at a fine capillary. The tube was then connected to the side-arm of the distillation flask by pressure tubing, the apparatus was exhausted, the capillary tube broken, and the carbon dioxide boiled over into the receiver. The method serves to characterise enzymes and yeasts by fermenting with them appropriate sugars.

E. H. R.

**Analysis of Silicate and Carbonate Rocks.** W. F. HILLEBRAND (*U.S. Geol. Survey, Bull.* 700, 1919, 1—285).—The Bulletin is a general treatise on the analysis of rocks; methods are described for the separation and estimation of the common and rare constituents of the rocks, and only those methods which have been found to be trustworthy are recommended. Attention is directed to the frequent occurrence of boron in rocks, but hitherto the estimation of this element has usually been neglected; Chapin's method (A., 1909, ii, 93) is recommended for the purpose.

W. P. S.

**The Analysis of Natural Silicates.** LOUIS DUPARC (*Bull. Soc. franç. Min.*, 1919, 42, 138—241; from *Chem. Zentr.*, 1920, ii, 680).—A summary and extension of many scattered communications by the author and his pupils on this subject. The work comprises a critical re-examination, discussion, and frequently modification of practically all the important methods of silicate analysis.

H. W.

**Practical Methods for the Estimation of Radium. III.  $\alpha$ -Ray Method,  $\gamma$ -Ray Method, Miscellaneous.** S. C. LIND (*J. Ind. Eng. Chem.*, 1920, 12, 469—472. Compare A., 1915, ii, 486; 1916, ii, 114).—The  $\alpha$ -ray method is simple and sufficiently trustworthy for many purposes, but it cannot take the place of a direct radium estimation in such minerals as carnotite, pitchblende, etc. The errors are due to variation in the amount of the loss of radium emanation by gaseous diffusion from the ore, to variation in the radium-uranium ratio, and to the position of the radioactive material in the individual grains of the ore. The  $\gamma$ -method is a convenient means of measuring radium in quantities above 0.1 mg., but the radium preparation must be confined in a closed vessel for one month before the measurement is made, so that the

$\gamma$ -radiation will have reached a maximum; if the measurement is made earlier a correction must be made for the unelapsed time. Modifications of the interchangeable electroscope (*loc. cit.*) are described.

W. P. S.

### **The Separation and Gravimetric Estimation of Potassium.**

S. B. KUZIRIAN (*Proc. Iowa Acad. Sci.*, 1917, **24**, 547—550).—Aniline perchlorate is the best reagent to replace platinic chloride for the separation and gravimetric estimation of potassium. The best results are obtained when the following points are observed: The exact strength of alcohol used must be known, and none used that runs below 99.5%. For every 1.5 c.c. of water used for dissolving the mixed chlorides, 50 c.c. of absolute alcohol should be used. The solution of a weighed amount of aniline perchlorate in 50 c.c. of absolute alcohol is added to the solution of the mixed chlorides drop by drop with constant shaking and set aside for one to two hours before filtering, to avoid occlusion of potassium chloride. The chief objections to the perchlorate method are the time and the slight solubility of potassium perchlorate in 95% alcohol. The use of aniline perchlorate in place of perchloric acid so shortens the process as to render it more advantageous than any other method in use for the separation and estimation of potassium; moreover, it affords the best means for the direct separation and estimation of sodium in the alcoholic filtrate.

CHEMICAL ABSTRACTS.

**The Carrying Down of Calcium and Magnesium Hydroxides by Precipitates of Ferric Hydroxide.** TOPORESCU (*Compt. rend.*, 1920, **170**, 1251—1253).—A second precipitation with ammonium hydroxide is quite sufficient to remove all calcium hydroxide from a ferric hydroxide precipitate. This may also be effected by washing the first precipitate of ferric hydroxide with a boiling 5% solution of ammonium nitrate. The addition of 2% of ammonium chloride to the solution prior to the precipitation of ferric hydroxide does not prevent it from carrying down some calcium hydroxide. Similarly, it does not prevent the carrying down of magnesium hydroxide, and the latter cannot be removed either by simple reprecipitation of the ferric hydroxide or by washing the precipitate with ammonium nitrate. W. G.

**Estimation of Mercury.** C. M. BOUTON and L. H. DUSCHAK (*U.S. Bureau of Mines, Techn. Paper*, **227**, 1920, 1—44).—The finely powdered mercury ore is mixed with lime and heated in a tube closed at one end. A layer of coarse sand is first placed in the tube, then the mixture, and finally a layer of lime, and the opening closed with a plug of brass wire gauze. The tube is allowed to project 7 to 12 cm. beyond the furnace, which is heated at about 500°. The effect of the sand filling is to reduce the volume of air expelled, and so prevent loss of mercury. In the presence of much sulphur, cupric oxide is mixed with the lime, whilst organic matter is oxidised by adding a small proportion

of potassium chlorate to the sand. The distilled mercury is dissolved off the tube by hot nitric acid, and oxidised by means of potassium permanganate, the excess of which is removed with hydrogen peroxide, and the solution titrated with standard potassium thiocyanate solution, with ferric sulphate or nitrate (free from haloids) as indicator. The method is also applicable to mercury in solution, the metal being precipitated as sulphide, and the precipitate treated as described. [See, further, *J. Soc. Chem. Ind.*, 1920, 492A.]  
C. A. M.

**Petersen's Method for the Qualitative Separation of Cations of the Third and Fourth Groups.** P. DE PAUW (*Chem. Weekblad*, 1920, 17, 191—192).—Various imperfections in Petersen's scheme (A., 1910, ii, 654) are pointed out and discussed. The following alternative scheme is proposed: To the acid hydrogen sulphide filtrate sodium sulphate solution is added, whereby barium, strontium, and calcium (in part) are removed as sulphates. The filtrate contains the ions  $\text{Fe}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Cr}^{+++}$ ,  $\text{Al}^{+++}$ ,  $\text{Zn}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ . This is treated with solid sodium carbonate and sodium hydroxide. Ammonia is boiled off, and sodium sulphide added. All metals except aluminium are precipitated as carbonates, hydroxides, or sulphides. Dilute hydrochloric acid removes  $\text{Fe}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Cr}^{+++}$ ,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$  as chlorides, leaving nickel and cobalt as sulphides. To this solution is added solid sodium carbonate and sodium hypochlorite. Zinc and chromium form zincoxide and chromate respectively, which may be separated by means of barium chloride. The residue contains ferric hydroxide, hydrated manganese dioxide, calcium and magnesium carbonates. This is treated with 5% acetic acid containing a little phosphate. A solution of calcium and magnesium acetates is obtained. The residue is dissolved in sodium peroxide and nitric acid, and the iron and manganese separated in the usual way.

W. S. M.

**Different Methods of Estimation of Manganese and their Use in the Examination of Plant Ashes and Similar Products.** D. H. WESTER (*Rec. trav. chim.*, 1920, 39, 414—422).—For the estimation of small amounts of manganese a colorimetric method is necessary, and of the four methods examined only one, namely, that of Marshall (compare A., 1901, ii, 350), in which the manganese is oxidised to permanganate by potassium persulphate, is found to be satisfactory. The presence of small amounts of nitric or sulphuric acid or silver nitrate do not interfere with this method. The amount of persulphate used has no influence. The heating in a water-bath for the oxidation should not exceed thirty minutes. The presence of salts likely to be found in plant ashes does not interfere with the estimation, although it is preferable to remove chlorides by a preliminary evaporation with sulphuric acid. If ferric salts are present to an extent of more than 0.05 gram per 100 c.c., they may make it impossible to carry out the

colorimetric comparison, and thus the method may not always be applicable to the analysis of soils. W. G.

**Separation of Chromium and Manganese.** M. HERSCHKOWITSCH (*Zeitsch. anal. Chem.*, 1920, **59**, 11—12).—The manganese and chromium are oxidised to permanganate and chromate respectively, and their solution is heated on a water-bath for some hours with the addition of ammonium sulphate and an excess of ammonia. The chromate remains unchanged, whilst the whole of the manganese is precipitated; the precipitate is collected, washed with 5% ammonium sulphate solution, then with hot water, ignited, and weighed as  $Mn_3O_4$ . W. P. S.

**Separation of Tin and Antimony. Estimation of Tin by Cupferron.** A. KLING and A. LASSIEUR (*Compt. rend.*, 1920, **170**, 1112—1114).—The antimony is separated from the tin by precipitation with hydrogen sulphide in the presence of hydrofluoric acid. The antimony sulphide is collected, washed, and redissolved in hydrochloric acid with a little potassium chlorate. The solution is filtered, and the antimony reprecipitated as its sulphide, which is collected, dried at  $300^\circ$  in a current of carbon dioxide, and weighed.

To the filtrate from the first precipitation of the antimony sulphide, boric acid is added, and the liquid boiled with a little hydrogen peroxide. After cooling, a 10% solution of cupferron is added, and the white precipitate which forms is collected, washed with cold water, dried, and calcined, and the tin weighed as stannic oxide. The results obtained by this method are very satisfactory. [See, further, *J. Soc. Chem. Ind.*, 1920, 470A.]

W. G.

**Estimation of Ethyl Alcohol in Mixtures of Alcohol, Sulphuric Acid, and Water.** G. S. BUTLER and H. B. DUNNICLIFF (*J. Soc. Chem. Ind.*, 1920, **39**, 146—147T).—The free acid, that is, free sulphuric acid plus acidity due to ethyl hydrogen sulphate, is determined by direct titration with standard alkali. The total acid present, including that which has undergone esterification, is determined by evaporating a weighed quantity of the alcoholic sulphuric acid with excess of standard alkali to a pasty consistence, heating in an air oven for half an hour at  $120^\circ$ , extracting with distilled water, and titrating the excess alkali with standard acid. By a simple calculation, from the two determinations, the acid esterified, and hence the alcohol present as ester, can be found. The free alcohol is determined by distillation, followed by a density determination of the filtrate. E. H. R.

**The Action of Hydrocyanic Acid on Dextrose.** J. BOUGAULT and J. PERRIER (*Compt. rend.*, 1920, **170**, 1395—1397).—The action of potassium cyanide on dextrose may be used as a means of estimating dextrose if an excess of the cyanide is used and the mixture is left for at least two days at  $20^\circ$  as the action is slow.

The residual excess cyanide may then be estimated, or the change in rotation, from  $[\alpha]_D + 53^\circ$  of the dextrose to  $[\alpha]_D + 1.87^\circ$  of the glucoheptonates, may be determined.

If an excess of sugar is used with a deficiency of cyanide, the whole of the cyanide is destroyed in about ten hours at  $20^\circ$ , and the mixture is no longer toxic.

W. G.

**An Improved Method for the Estimation of Sugar in the Urine and Blood.** P. J. CAMMIDGE (*Lancet*, 1919, 1, 939).—

Further experience with the volumetric method for the estimation of sugar (*A.*, 1917, ii, 276) has confirmed the accuracy of the results given with quantities above 0.5%, but with percentages below that amount too low a reading may be obtained unless further precautions than those described are taken against oxidation, especially in warm weather. When a urine is expected to contain a low percentage of sugar, under 0.5%, and with all blood and other fluids containing smaller amounts, the water to which the iodine solution is to be added should be thoroughly boiled, to expel dissolved air, and cooled immediately before the estimation is to be made. It is also advisable that the alkaline copper solution for sugar estimations with urine be boiled in a small conical flask, provided with a loose funnel as a stopper, instead of in a beaker as previously described, and that the required amount of urine be run into the boiling fluid from a pipette when the air dissolved in the solution and contained in the flask has been expelled. With blood, etc., the 7.5 c.c. of filtrate and 1 c.c. of modified Benedict solution are added after they have boiled for a few seconds. The water used for diluting the iodine solution and for washing out the flasks, etc., should have been recently boiled and cooled. With these additional precautions the method gives uniformly trustworthy figures, even with the small amount of sugar in normal urine and blood.

CHEMICAL ABSTRACTS.

**Proximate Analysis of Coniferous Woods.** W. H. DORE (*J. Ind. Eng. Chem.*, 1920, 12, 476—479).—Methods are given for the estimation of loss on drying benzene extract, alcohol extract, cellulose, lignin, soluble pentosans, mannan, and galactan. Preliminary hydrolysis is omitted in the estimation of the cellulose and lignin; soluble pentosans are estimated in the chlorination liquors, and mannan and galactan on separate portions of the original material. Analyses of redwood, yellow pine, and sugar pine show that the sum of the constituents, as found by the above-mentioned methods, is slightly over 100% in every case.

W. P. S.

**Colorimetric Estimation of Lactic Acid in Urine.** POLONOWSKI (*Compt. rend. Soc. Biol.*, 1920, 73, 475; from *J. Pharm. Chim.*, 1920, [vii], 21, 449—450).—The urine is clarified by adding from 1 to 3% of egg-albumin and precipitating this with sodium metaphosphate and dilute sulphuric acid. One c.c. of the clear urine is then treated with 5 c.c. of concentrated sulphuric

acid (added slowly to prevent heating) and 5 drops of a 1% codeine solution (in alcohol), and the yellow coloration obtained is compared with those of standards containing known amounts of lactic acid. The results are trustworthy only when not less than 0.001% or not more than 0.01% of lactic acid is present. W. P. S.

**Identification of the Cinnamic Ion by means of the "Oxyferric" Catalyst [a Ferric Salt + Hydrogen Peroxide].**

G. DENIGÈS (*Bull. Soc. pharm. Bordeaux*, 1919, **57**, 209—212).—In the case of free cinnamic acid or a cinnamate, as little as 0.02 gram of the acid in 1 litre of solution can be detected by adding 1 drop of ferric chloride solution to 2 c.c. of the solution to be tested, boiling, and adding 1 drop of hydrogen peroxide (6—10 vols. oxygen), when the odour of benzaldehyde is observed after shaking for about ten seconds. The sensitiveness of the reaction is increased by adding 1 drop of 10% sulphuric acid with the ferric chloride solution; this procedure also serves for the identification of a cinnamate. In the case of a cinnamic ester one drop (if liquid) or several particles (if solid) of the sample is boiled for twenty to thirty seconds with 6—8 c.c. of dilute sodium hydroxide solution; the solution while hot is acidified with 10% sulphuric acid, 1 drop of ferric chloride solution is added, the mixture is boiled, treated with 1 drop of hydrogen peroxide solution, and again boiled, whereby the odour of benzaldehyde is produced. This method also serves to detect the presence of cinnamic acid in complex mixtures, such as Peru and Tolu balsams.

CHEMICAL ABSTRACTS.

**Estimation of Salicylic Acid in the Blood and its Action on the Heart.** C. FRIDERICHSEN (*Arch. expt. Path. Pharm.*, 1917, **80**, 235—259).—A micro-method for the estimation of salicylic acid in blood. The blood is absorbed by a small piece of blotting paper (about 250 mg.), and weighed in a torsion balance. The paper is then introduced into a test-tube, to which 10 c.c. of a boiling solution of calcium chloride containing 1.5 c.c. of 25% hydrochloric acid per litre is added. It is allowed to remain in contact with the solution for three hours. The calcium chloride solution is extracted with ether. The ether is just evaporated on a water-bath at 32—33°, and any traces left removed by means of a stream of air. The salicylic acid is dissolved in water and estimated colorimetrically. Employing this method the distribution of salicylic acid in the serum and in the blood corpuscles, as well as the action of various doses on the heart, was studied, the results of which are recorded in the communication. S. S. Z.

**Two Procedures for the Estimation of Alkali Nitroprussides.** LE HER (*Bull. Soc. pharm. Bordeaux*, 1920, **58**, 12—16).—A solution of 1.0 gram of sodium nitroprusside in 50 c.c. of water is filtered and 59 c.c. (*sic*) of the filtrate are neutralised with sulphuric acid and treated with an excess of a ferric salt. The precipitate of Prussian blue is collected, washed with hot water

(these washings are discarded), then several times with a 20% sodium hydroxide solution, and again with water, the combined filtrates containing sodium ferrocyanide are acidified with sulphuric acid and titrated with 0.1*N*-permanganate (1 c.c. = 0.03582 gram of sodium nitroprusside).

In the second method a solution containing not more than 0.40 gram of sodium nitroprusside is treated in a 100 c.c. flask with 30 c.c. of 0.1*N*-silver nitrate, water is added to the mark, and, after shaking, the liquid is filtered and the excess of silver nitrate in the filtrate and washings is estimated by Denigès' silver cyanide method.

CHEMICAL ABSTRACTS.

**Differentiation of Vanillin and Heliotropin.** A. LABAT (*Bull. Soc. pharm. Bordeaux*, 1919, 57, 259—260).—To 2 c.c. of sulphuric acid (D 1.84) are added 0.1 c.c. of an alcoholic solution of vanillin or heliotropin and 0.1 c.c. of an alcoholic solution of gallic acid (20%), and the mixture is boiled on a water-bath for two or three minutes. In the case of vanillin, the liquid will assume a yellowish-brown or brown colour, whereas the liquid containing heliotropin will be coloured blue or emerald-green, depending on the quantity of heliotropin present. This reaction serves to detect heliotropin in quantities as small as 0.00005 mg.

CHEMICAL ABSTRACTS.

**The Nitrosoindole Test.** J. GROENEWEGE (*Med. Geneesk. Lab., Weltevreden*, 1919, [iii], A, 177—193).—The red coloration obtained when a peptone culture of certain bacteria is treated with a drop of mineral acid is due to the presence of nitrate in the peptone, and there is no need to add nitrite before the coloration can be obtained. If the peptone medium is inoculated previously with a denitrifying organism, the nitrate is reduced to nitrite and the latter to ammonia or nitrogen, and the medium no longer yields a nitrosoindole reaction when used for the culture of the organisms mentioned (cholera vibrios, etc.). Conversely, the peptone medium freed from nitrate and nitrite as described may be used for the detection of traces of nitrate; the substance to be tested is added to the medium, which is then inoculated with an organism capable of giving a nitrosoindole reaction. W. P. S.

**Analytical Characters of Dimethylaminoantipyrine (Pyramidone).** JUAN A. SÁNCHEZ (*Anal. Soc. Quim. Argentina* 1918, 6, 422—428, 513—521).—Various oxidising agents impart a violet colour to solutions of pyramidone. The action of iodic acid is quantitative, each atom of oxygen acting on one molecule of pyramidone; when a solution of the base is treated with excess of iodic acid, iodine is liberated after a few minutes. By means of this reaction the purity of pyramidone may be determined colorimetrically; 0.5, 1, 1.5, 2, 2.5, and 3 c.c. of a 0.1% solution of standard pyramidone are treated in cylinders with water to 3 c.c. bulk, one drop of concentrated sulphuric acid, and 2 c.c. of 1% iodic acid solution. After five minutes, 5 c.c. of chloroform are added to



each tube, and the liquid well shaken. The sample to be tested is treated in the same manner, and the intensity of the violet colour of the liberated iodine in chloroform in each series of tubes compared.

Antipyrine is without action on iodic acid, but absorbs iodine; an admixture of 20% of antipyrine is sufficient to prevent the liberation of iodine by pyramidone. Distillation of pyramidone with ferric chloride or the theoretical amount of iodic acid yields formaldehyde, derived from the oxidation of a methyl group. To detect pyramidone in presence of large quantities of antipyrine, *N*/10-silver nitrate is recommended. This produces after five minutes in the cold, but quickly on warming, an intense bluish-violet coloration.

Pellizzari's reaction (combination of antipyrine with formaldehyde) can be used for the quantitative separation of antipyrine and pyramidone; 5 c.c. of the aqueous solution of the two bases are left for four days with 5 c.c. of formaldehyde, 2 c.c. of hydrochloric acid, and 2 c.c. of water; the liquid is made ammoniacal, when a precipitate of methylenediantipyrine is obtained. The filtrate is treated with chloroform to extract pyramidone.

To detect small quantities of antipyrine in pyramidone, a little of the powder in a porcelain dish is submitted to the action of nitrous fumes from sodium nitrite and sulphuric acid; the antipyrine crystals will acquire a persistent green colour, whilst pyramidone is coloured violet, although only transiently. To prove the presence of pyramidone in coloured or syrupy liquids, 10 c.c. are made alkaline with ammonia and shaken with chloroform. The separated extract is evaporated to dryness, and the residue dissolved in water and tested with silver nitrate. Pyramidone may be titrated with *N*/10-sulphuric acid in presence of methyl-orange, 0.231 gram of pyramidone requiring 10 c.c. of the acid for neutralisation.

W. R. S.

**Excretion of Quinine in the Urine.** M. NIERENSTEIN (Extract from Observations on Malaria, War Office, 1919, pp. 1—79. Compare A., 1919, i, 236).—The thalleioquinine test can only be regarded as a valuable positive test for quinine, a negative result in no way indicating the absence of the drug. Many other qualitative tests for quinine were investigated, but the only one which is regarded as quite trustworthy is Ramsden and Lipkin's technique for carrying out Herepath's test. Encouraging results were obtained with Robertson's test. In testing for quinine in urine the picric acid test is recommended for clinical use.

The estimation of quinine in urine was studied very completely, and the author obtained the best results with Barratt and York's modification of Giemsa and Schaumann's method. By this method the excretion of quinine was fully studied.

J. C. D

## General and Physical Chemistry.

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**Secondary Spectrum of Hydrogen.** MEGH NAD SAHA (*Phil. Mag.*, 1920, [vi], **40**, 159—161).—A reconsideration of the calculations of Fabry and Buisson (A., 1912, ii, 613) leads to the conclusion that if the  $H\alpha$  line is emitted by a hydrogen atom, the secondary lines are emitted by the hydrogen molecule. J. R. P.

**Structure of the Balmer Series of Hydrogen Lines.** T. R. MERTON (*Proc. Roy. Soc.*, 1920, [A], **97**, 307—320).—The  $H\alpha$  and  $H\beta$  lines have been examined by means of an échelon diffraction grating of thirty-five plates, 15.085 mm. thick, and with a grating step of 0.83 mm. The light was subjected to a preliminary analysis by means of a constant deviation spectroscope before passing into the échelon. It is shown that in tubes containing hydrogen and helium at a few millimetres pressure, the resolution of  $H\alpha$  is complete, whilst  $H\beta$  shows no definite structure. On cooling the spectrum tube with liquid air, the  $H\alpha$  line appears as a sharp doublet, perfectly resolved, and  $H\beta$  also appears as a definite doublet, but the components are not completely resolved and are hazy in appearance. In the case of the  $H\alpha$  doublet, the separation of the components is 0.1446 Å, and the intensities of the components are in the ratio 10:4.6, whilst for  $H\beta$  the separation is 0.093 Å. The half-width of the components is  $H\alpha$ , 0.028 Å;  $H\beta$ , 0.045 Å. The author is of the opinion that the observations cannot be explained on the basis of simple doublets, and that it is probable that these lines consist of three or more components, which show great variability in their relative intensities under different conditions. J. F. S.

**Spectra and Atomic Numbers of the Elements.** J. E. PAULSON (*Astrophys. J.*, 1919, **49**, 276—281).—Rydberg's relation between the frequency-difference of certain spectral lines and the atomic weight,  $10^3\nu/P^2$ , where  $\nu$  is the frequency-difference and  $P$  the atomic weight, is based on a unit which is not fundamental, and the substitution of atomic number for atomic weight gives a better relation. Taking Rydberg's atomic numbers ( $E=0$ ,  $H=1$ ,  $?=2$ ,  $?=3$ ,  $He=4$ ,  $Li=5$ , etc.), frequency-differences are calculated on the basis of the two formulæ,  $\nu=A \log (N+n)+B$  and  $\nu=A \log (P+n)+B$ , where  $N$  is the atomic number,  $A$  and  $B$  are constants computed by the method of least squares, and  $n$  is a whole number, generally small, which may be positive or negative. For the groups of metals examined, the formula for atomic numbers agrees much better with observed frequencies.

CHEMICAL ABSTRACTS.

**Atomic Theory and Low Voltage Arcs in Cæsium Vapour.**

PAUL D. FOOTE and W. F. MEGGERS (*Phil. Mag.*, 1920, [vi], **40**, 80—97; *J. Opt. Soc. Amer.*, 1920, **4**, 145—147).—The normal operation of an arc below ionisation may result in the excitation of a single-line spectrum, a single-series spectrum, or a group spectrum consisting of lines of different series. An explanation is offered of fluorescence in vapours of alkali metals. A mechanism of absorption of radiation is described. The cæsium spectrum was photographed for various accelerating voltages from  $\lambda$  3878 to  $\lambda$  9208 with plates stained with dicyanin. No evidence of group or single-series spectra was found. The doublet,  $1\cdot5s-2p_{\frac{1}{2}}$  is alone produced under excitation of 1·5 to 3·9 volts accelerating field. The intensity of these lines gradually increases approximately in proportion to the total number of electrons reaching the anode until the ionisation potential is reached. At this point, a pronounced decrease in intensity occurs, this decrease taking place at the voltage at which the complete line spectrum is produced. This affords a strong argument for Bohr's theory. After a certain voltage, the intensity of any line per unit number of electrons reaching the anode attains a saturation value, in agreement with the quantum hypothesis. Only two types of inelastic impact between electrons and atoms of the alkali metal vapours occur, at the resonance and ionisation potentials respectively, and given by the quantum relation  $h\nu = eV$ , where  $\nu = 1\cdot5s-2p_1$  and  $\nu = 1\cdot5s$ .

J. R. P.

**Extreme Ultra-violet Spectra of Magnesium and Selenium.**

J. C. McLENNAN, J. F. T. YOUNG, and H. J. C. IRETON (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 67—72).—The spectrum of magnesium for spark in air and arc in air has been investigated in the region between 2026 and 1850 Å.U., and seven new lines recorded. The spectrum of the magnesium arc in a vacuum has been investigated in the region between 2300 and 1400 Å.U., and seven new lines measured. Several of these agree with lines found by Saunders with the spark in hydrogen, and by Handke with the spark in air. The series  $\nu = (1\cdot5s) - (m, p)$  has been verified for values of  $m$  from 2 to 6, but experiments have failed to detect any further lines of the series  $\nu = (1\cdot5s) - (m, p_2)$ , beyond, possibly, the second member. Thirty lines have been recorded in the selenium arc spectrum between 2300 and 1400 Å.U.

J. R. P.

**Metallic Spectra Produced in High Vacua.**

EDNA CARTER and ARTHUR S. KING (*Astrophys. J.*, 1919, **49**, 224—236).—Spectra of manganese, titanium, iron, magnesium, calcium, and cadmium were produced by vaporising the metals at the focus of a beam of cathode rays and photographing the luminescence in the path of the rays. The metallic vapour in all cases except iron assisted the evacuation by absorbing gas molecules, but iron did not, and in order to vaporise it, it was necessary to make the anticathode

the anode. The lines excited were generally those of the arc and furnace spectra, with the following peculiarities: Certain arc and furnace lines are intensified, whilst others are weakened or absent. The tendency to give enhanced lines, that is, the resemblance to the arc spectrum, is marked in the case of cadmium, present also in the cases of magnesium and calcium, but is very slight for iron, manganese, and titanium. Single-line series show a relatively greater intensity than other series lines. The intensity of the ultra-violet lines is relatively high as compared with the arc and furnace spectra.

CHEMICAL ABSTRACTS.

**Arc Spectrum of Cobalt According to International Normals.** FERDINAND DHEIN (*Zeitsch. Wiss. Photochem.*, 1920, **19**, 289—335).—The arc spectrum of cobalt has been measured by means of a concave grating 6.54 metres radius and 20,000 lines per inch. Granular cobalt was placed in a carbon arc burning with a current of 4—6 amps. at 150 volts, and served as the source of light in all measurements. An iron arc was used for the comparison spectrum. The wave-lengths and intensities of 1,384 lines between  $\lambda$  7417.38 and  $\lambda$  2590.606 are recorded in tables and compared with measurements of Krebs (*Diss. Bonn*, 1916). The lines due to impurities, nickel, iron, manganese, calcium, copper, silver, titanium, aluminium, magnesium, and vanadium are recorded in other tables.

J. F. S.

**Absorption Spectra of Thallium, Aluminium, Lead and Tin, and Arsenic.** J. C. McLENNAN, J. F. T. YOUNG, and H. J. C. IRETON (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 7—13).—In addition to the absorptions of thallium discovered by Guthrie (*Diss. Baltimore*, 1908), further absorptions were obtained as arc reversals. These additional absorptions in the ultra-violet region were confined to the two series,  $\nu = (2, p_2) - (m, d')$  for values of  $m = 6$  to 14 inclusive, and  $\nu = (2, p_2) - (m, s)$  for  $m = 5.5$  to 11.5 inclusive. The series  $\nu = (2, p_2) - (m, s)$  has been observed for values of  $m = 10.5$  and  $m = 11.5$  for the first time. No absorption was obtained in the region 1700 Å.U. with the thallium arc in a vacuum. The absorption spectrum of aluminium consists of fourteen bands in the extreme ultra-violet. As with thallium, these absorptions are given by the series,  $\nu = (2, p_2) - (m, d')$  for values of  $m = 6$  to 14 inclusive, and  $\nu = (2, p_2) - (m, s)$  for values of  $m = 4.5$  to 8.5 inclusive. The series  $\nu = (2, p_2) - (m, d')$  has been verified for  $m = 12, 13$ , and 14, and the series  $\nu = (2, p_2) - (m, s)$  for  $m = 6.5$  and 7.5, for the first time. In all, nineteen absorption bands of lead were measured. It is possible that the system of narrow and diffuse absorptions may correspond with the analogous series absorptions of thallium and aluminium. Three absorption bands of tin were obtained, but no identification of series is yet possible. The flame spectrum of arsenic consists of five lines: 3266, 2860, 2780, 2350, and 2288 Å.U., together with four bands with heads at 2634.5, 2570, 2503.5, and 2437.3 Å.U. The arc absorption spectrum con-

sists of four strong unilateral bands, the sharp edges of which were towards the red, and occurred at wave-lengths 2634·5, 2570·0, 2503·5, and 2437·31 Å.U. Contrary to expectation, no single-line absorption or emission was found which could possibly be supposed to correspond with the line 2620 Å.U. predicted by Foote and others.

J. R. P.

**The Absorption Spectra of the Cobalt Dithiocarbamates and Xanthates.** MARCEL DELÉPINE and LOUIS COMPIN (*Bull. Soc. chim.*, 1920, [iv], 27, 474—477).—A comparative study of the absorption spectra of certain of the cobalt xanthates and dithiocarbamates previously described (this vol., i, 522, 536) shows that, from the point of view of absorption, the group  $\cdot\text{CS}\cdot\text{S}\text{]}_3\text{Co}$  dominates all the singularities of the rest of the molecule.

W. G.

**Absorption of Light by Methæmoglobin in Neutral Solution and in Solution made Alkaline by Sodium Carbonate.** PAUL HÁRI (*Biochem. Zeitsch.*, 1920, 103, 271—292).—There is a marked difference in the spectroscopic behaviour of methæmoglobin in neutral solution and in solution made alkaline by sodium carbonate. It is suggested that in alkaline solution, methæmoglobin is reconverted into oxyhæmoglobin, and is probably also changed into other hæmoglobin derivatives.

S. S. Z.

**Light Absorption and Fluorescence. VI. Atomic and Molecular Energy Quanta. VII. Molecular Phases.** E. C. C. BALY (*Phil. Mag.*, 1920, [vi], 40, 1—14, 15—31. See A., 1915, ii, 605; 1916, ii, 240).—VI. From the conception of the elementary energy quantum required to shift one electron from one stationary orbit to another, and the simple assumption that the combining atoms share equally in the energy loss on combination and in the future energy changes of the resulting molecule, the author arrives at the conception of molecular quanta and molecular frequency, the latter being the least common multiple of the atomic frequencies. The smallest possible equal amounts of energy which two or more atoms can evolve when combining together are equal to one quantum measured at the frequency which is the least common multiple of their atomic frequencies. The molecule may also exhibit those frequencies which are characteristic of its component atoms. These conceptions are applied to the elucidation of the observed relationships between the absorption frequencies of compounds.

VII. Chemical reactivity of atoms is due to the attraction exerted by their electromagnetic fields. As a result of this attraction, an additive complex is formed as a first stage in the reaction. The second stage is the joint loss by all the atoms of equal amounts of energy, and the formation of a freshly synthesised molecule with its infra-red fundamental. The reactivity of molecules is a function of their force fields, and the first stage of any reaction between two or more molecules is the formation of an additive

complex, due to the attraction of their force fields. The reactivity of a molecule will depend on the molecular phase in which it exists; the greater the condensation which has occurred in the force field, the less will be the reactivity. J. R. P.

**The Photochemical Equivalent Law from the Point of View of the Bohr-Einstein Conception of Light Absorption.** O. STERN and M. VOLMER (*Zeitsch. wiss. Photochem.*, 1920, 19, 275—287).—A theoretical paper in which the discrepancy between the Einstein equivalent law  $n = E/h\nu$  is explained by means of Bohr's conception of light absorption. J. F. S.

**Mathematical Theory of Photochemical Kinetics.** J. PLOTNIKOV (*Zeitsch. wiss. Photochem.*, 1920, 19, 225—274, 335—348).—A mathematical paper in which, after a general introduction to photochemical kinetics, the author develops the kinetic relationships of irreversible photochemical reactions for the normal case where there is a moderate absorption of light, and also for the limiting cases where there is, respectively, a very strong and a very weak absorption of light. The special cases of polychromatic light, mirror action, and also reactions with circulating reagents and those occurring in cylindrical vessels, are considered, and mathematical relationships developed for them. Reactions which occur in laminæ are dealt with, and the conditions are established for filter action, both internal and external. The author also considers photo-reactions which are accompanied by non-photochemical reactions, and reactions of one photo-active component for the conditions (a) where there are two separated photo-active absorption bands, and (b) where there are two partly superposed photo-active absorption bands. The case of two active components is considered (a) where one component is photo-active and the other is not, and (b) where both components are photo-active. The influence of temperature and the order of photochemical reactions are treated, and, finally, the special case is discussed where an inactive component constitutes a light filter. J. F. S.

**The Action of Phosphorus, during Oxidation, on the Photographic Plate and its Ionising Power.** W. P. JORISSEN (*Rec. trav. chim.*, 1920, 39, 429—434).—A reply to Centnerszwer and Petrikal'n (compare A., 1912, ii, 709). W. G.

**The Cleavage of Lactic Acid by Rays of Short Wave-lengths.** OSKAR BAUDISCH (*Biochem. Zeitsch.*, 1920, 103, 59—63).—The author could not confirm Euler's observation that, on exposing lactic acid to the light of a quartz mercury vapour lamp, alcohol is formed (A., 1911, ii, 452; 1912, ii, 407), nor could he confirm the formation of methane by this exposure, as was alleged by Schanz (*Arch. ges. Physiol.*, 1918, 71, 650). Acetone, according to the author, does not form methane and acetic acid by being exposed in dilute aqueous solution to sunlight for a short time. These products are formed after an exposure of several months. S. S. Z.

**Action of Radiations of Different Wave-lengths on Chlorophyll.** RENÉ WURMSER (*Compt. rend.*, 1920, 170, 1610—1612).—In the action of light on chlorophyll in acetone solution in the red, green, and violet portions of the spectrum, it is shown that the photochemical susceptibility varies with the wave-length in a manner proportional to the constant of absorption, except in the neighbourhood of the minimum of absorption, where it decreases more rapidly. The radiations, the frequencies of which correspond with the two principal bands, red and violet, of the chlorophyll, are, for equal absorbed energy, equally active.

W. G.

**The Absorption of X-rays.** R. A. HOUSTON (*Proc. Roy. Soc. Edin.*, 1920, 40, 34—42).—An expression used to denote the variation of the coefficient of absorption through an absorption band in optics is applied to the absorption bands of the *J*-, *K*-, and *L*-homogeneous *X*-radiation, and it is shown that from it can be deduced the number of electrons per atom taking part in the production of the radiation. The seven results given for *K*-rays do not differ greatly from unity, which is the same result as was deduced similarly by the author for the absorption bands of aniline colouring matters and inorganic salts (*Proc. Roy. Soc.*, 1909, [A], 82, 606). The mean value by one method of calculation is 0.972, and by another 1.01. For the *L*-bands of platinum and gold, the bands appear to be double with either one or two electrons concerned per component, that is, 2 or 4 in all. But for the *J*-bands the result (0.002 for aluminium) suggests that a singly charged hydrogen atom or doubly charged helium atom rather than an electron is the operative cause. The results furnish an independent confirmation of the wave-length of the *X*-rays, and tell against Bohr's model.

F. S.

**The Law of Mass-Absorption of the Röntgen Rays.** F. BUTAVAND (*Ann. Physique*, 1920, [ix], 13, 161—168).—An empirical and approximate relation is shown to hold between the mass-absorption coefficient  $\lambda/\rho$ , where  $\lambda$  is the absorption coefficient and  $\rho$  the density, and the atomic weights  $P_E$  of the emitting element and  $P_A$  of the absorbing element, which, deduced step by step for each series of rays, takes the general form

$$(\lambda/\rho)_n^{1/5} \times P_E/P_A^{1/2} = 13 + 2^{2(n-1)};$$

*n* refers to the type of radiation, and has for the four series *H*, *J*, *K*, *L* the values 1, 2, 3, 4 respectively.

In the table, the first column refers to the type of radiation, the second to the value of *n*, the third to the experimental value of the above expression on the left-hand side of the above equation, and the fourth to that calculated from the right-hand expression.

<i>H</i> .....	<i>n</i> =1	14	14
<i>J</i> .....	2	17	17.5
<i>K</i> .....	3	29	26
<i>L</i> .....	4	77	77

A graphical representation of these results leads to the suggestion that there exist two series to be discovered, designated *G* and *M*, the first very "hard" with the value in the last column corresponding with 13.25, and the second very "soft" with the value 270.

F. S.

**The Measurement of Radium Emanation in Spring Waters.** H. GREINACHER (*Physikal. Zeitsch.*, 1920, **21**, 270—272).—A method is described of carrying out the measurements of radium emanation in spring waters by means of small vessels, of 2 litres capacity or less, in place of the large 10- or 15-litre vessels usually employed. The volume of water,  $V_2$ , put into a can of volume  $V$  is arranged to be equal to  $V/(1 + \sqrt{\alpha})$ , where  $\alpha$  is the absorption coefficient of the emanation in water. After shaking, the water is run out and fresh air admitted to take its place. The emanation in the vessel is then measured. Particulars are given for the reduction of the results to Mache units.

F. S.

**New Determination of the Absolute Value of the Radium: Uranium Ratio.** S. C. LIND and L. D. ROBERTS (*J. Amer. Chem. Soc.*, 1920, **42**, 1170—1177).—A standard radium solution was prepared by dissolving 0.2067 gram of 100% radium chloride containing 157.3 mg. of radium in 1 litre of 5% redistilled hydrochloric acid. The radium content of the specimen was controlled by the  $\gamma$ -ray method by comparison with the International radium standard. The clear solution was diluted with 5% hydrochloric acid until 1 litre contained  $1.573 \times 10^{-6}$  gram of radium, protected by one million times as much barium chloride. This standard solution was used to standardise three electroscope chambers, each of which had two interchangeable leaf chambers. The standardisation was effected by the Bureau of Mines method (emanation method). The same electroscopes were also standardised by the U.S. Bureau of Mines pitchblende standard. The results give as a final average of eighteen determinations,  $3.40 \times 10^{-7} \pm 0.03$  for the ratio radium:uranium. The result agrees with the results of Becker and Jannasch,  $3.399 \times 10^{-7}$  (*Jahrb. Radioaktiv. Elektronik.*, 1915, **12**, 1—34), and Rutherford and Boltwood,  $3.4 \times 10^{-7}$  (*A.*, 1905, ii, 568; 1906, ii, 593; 1908, ii, 454; 1914, ii, 788).

J. F. S.

**The Determination of the Radioactivity of Spring Waters.** OTTOMAR NÜRNBERGER (*Physikal. Zeitsch.*, 1920, **21**, 241—245).—Investigations were made on the radioactivity of a group of springs near Brambach, Saxony, by a variety of the special apparatus designed for this work. It was found that the rate of increase of the activity with time for the emanation was different for each spring and characteristic of it, and departed from that obtained for a solution of pure emanation. These differences are attributed to salts and gases dissolved in the natural spring water.

F. S.



**The Separation of Isotopes.** ALEXANDER FLECK (*Nature*, 1920, **104**, 565).—It is suggested, as a method of testing further the chemical separability of isotopes, that an ester, such as ethyl acetate, should be saponified with baryta containing radium and its isotope, mesothorium-1, and the ratio of the two isotopes estimated in the salt formed during the progress of the reaction. If the ratio is unchanged through the reaction, it will indicate that their reactive powers or strengths as bases are the same. F. S.

**Nomenclature Questions concerning Isotopes.** F. SEKERA (*Jahrb. Radioaktiv. Elektronik.*, 1920, **16**, 411—415).—A discussion of such terms as Misch elemente, element typus, and Bleiart in use in Germany in connexion with isotopes. F. S.

**Ionisation and Resonance Potentials of Nitrogen, Oxygen, and Hydrogen.** F. L. MOHLER and PAUL D. FOOTE (*J. Opt. Soc. Amer.*, 1920, **4**, 49—54).—The ionisation and resonance potentials have been measured for hydrogen, oxygen, and nitrogen by the methods previously used for the measurement of the critical potential of electron currents in metallic and non-metallic vapours (A., 1918, ii, 94, 287; 1919, ii, 42). In the case of nitrogen, by three methods, the resonance potential is found to be  $8.18 \pm 0.10$  volts, and the ionisation potential  $16.9 \pm 0.5$  volts. The resonance potential corresponds with the nitrogen doublet at  $\lambda = 1492.8 \text{ \AA}$  and  $\lambda = 1494.8 \text{ \AA}$ , whilst the ionisation potential corresponds with the first term of the series converging at  $\lambda = 730 \text{ \AA}$ . The resonance potential,  $7.91 \pm 0.1$  volts, was obtained for oxygen, and the ionisation potential has the value  $15.5 \pm 0.5$  volts. These values indicate that  $\lambda = 1570 \text{ \AA}$  is the single-line spectrum of oxygen and the first member of a series converging at  $\lambda = 800 \text{ \AA}$ . Hydrogen has a resonance potential at 10.4 volts, the first ionisation potential is 13.3 volts, and the second 16.5 volts. The first ionisation potential is for the atom and the second for the molecule, the difference should give the heat of dissociation per gram-molecule of hydrogen. This value is 74,000 cal., whereas Langmuir calculates the value 90,000 cal., and the value derived from Bohr's theory is 65,000 cal. The first ionisation potential is difficult to measure, and if the value be taken as 13.5, the value 65,000 cal. would then follow. There is evidence of a slight resonance collision between 2.5 and 3.5 volts, but the value has not yet been accurately fixed. J. F. S.

**Extrapolation of Conductivity Data to Zero Concentration. II.** EDWARD W. WASHBURN (*J. Amer. Chem. Soc.*, 1920, **42**, 1077—1087. Compare A., 1918, ii, 55).—The author's method of obtaining the value of  $\Lambda_\infty$  has been criticised by Kendall (A., 1918, ii, 182) and Kraus (this vol., ii, 217). In the present paper, the author discusses the points which have been criticised. In answer to Kendall's claim for priority, it is shown that the method used by Kendall is only possible when the electrolyte obeys the law of mass action, whilst the method under

discussion is possible, irrespective of whether the electrolyte obeys the law of mass action or not. In answer to Kraus, it is shown that the assumptions in the two cases are diametrically opposed. Mathematically expressed, Washburn writes

$$\lim_{c \rightarrow 0} 1/K_E \cdot dK_E/dC = 0,$$

whilst Kraus writes  $\lim_{c \rightarrow 0} 1/K_E \cdot dK_E/dC = -\infty$ .

J. F. S.

### Extrapolation of Conductivity Data to Zero Concentration.

CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1920, **42**, 1087—1090. Compare preceding abstract).—An answer to Washburn's paper (*loc. cit.*), in which it is shown that Washburn's results are a necessary consequence of the assumptions made. It is further shown that, whilst Washburn's method may be applicable to any form of curve and at any concentration, the value of  $\Lambda_0$  will be different for the different concentrations and for the different forms of curve, save in the exceptional case that  $\Lambda$  is a linear function of the concentration, in which case the law of mass action is actually obeyed.

J. F. S.

### Extrapolation of Conductivity Data to Zero Concentration.

EDWARD W. WASHBURN (*J. Amer. Chem. Soc.*, 1920, **42**, 1090—1091. Compare preceding abstracts).—An answer to Kraus, in which the author states that Kraus's criticism indicates that his method of extrapolation has been misunderstood. He therefore applies it to measurements of Wieland, and draws curves to show that, without using any assumption or smoothed curve, the value of  $\Lambda_0$  for potassium chloride lies at 129.65.

J. F. S.

**Theory of Electrolytic Ions. XVI. Electrical Conductivity of the Arsinic Acids.** RICHARD LORENZ and ERIKA SCHMIDT (*Zeitsch. anorg. Chem.*, 1920, **111**, 175—192. Compare this vol., ii, 482).—The electrical conductivity of arsanilic, *o*-aminotolylarsinic, diaminophenylarsinic, *m*-dihydroxyphenylarsinic, 3-nitro-4-aminophenylarsinic, dichlorophenylarsinic, 3-nitro-4-hydroxyphenylarsinic, *m*-nitrophenylarsinic, and phenylene-1:4-diarsinic acids have been determined at dilutions 1/64—1/1028, and the conductivity at infinite dilution has been extrapolated in each case. The conductivities of the following acids at infinite dilution have been obtained: arsanilic, 370.0; *o*-aminotolylarsinic, 369.0; diaminophenylarsinic, 369.0; *m*-dihydroxyphenylarsinic, 371.0; 3-nitro-4-aminophenylarsinic, 369; dichlorophenylarsinic, 371.0; 3-nitro-4-hydroxyphenylarsinic, 370.0; phenylene-1:4-diarsinic, 369.0; *m*-dinitrophenylarsinic, 369.0.

J. F. S.

**Measurement of Dielectric Constants using High Frequencies with a Wheatstone's Bridge.** HANS JOACHIM (*Ann. Physik*, 1919, [iv], **60**, 570—596).—The measurement of dielectric constants by means of a modified Hertwig apparatus is described (*ibid.*, 1913, **42**, 1099). It is shown that by the introduction of an ionic tube generator, it is possible to carry out the measurements with undamped waves of constant amplitude. The

apparatus is silent and very simple. In the same way, it is possible to use the Nernst method for measurements with rapid oscillations. A number of measurements with various substances are given as a test of the suitability of the method. The dielectric constant of potassium chloride (2.06), potassium alum (2.970), lead chloride (4.29), lead sulphate (3.72), lead formate (2.35), amorphous sulphur (2.84), mercuric chloride (2.58), mercuric cyanide (2.41), and ammonium sulphate (2.56) in the powdered condition has been determined; the values in these cases are indicated in brackets. The temperature-coefficient has been determined down to  $-180^{\circ}$  for several of the substances. The theory of the dependence of the dielectric constant on temperature, the rôle of the dielectric constant in electrolytic dissociation, the dependence of the dielectric constant on the wave-length, and its relation to the structure of the dielectric, are discussed. J. F. S.

### **The Electrostatic Potential of the Fluorspar Lattice.**

ELISABETH BORMANN (*Zeitsch. Physik*, 1920, 1, 55—56).—An error in the calculation of the electrostatic potential of the fluorspar lattice, as given by A. Lande, has led to errors in later calculations of other authors in which this value was used. Thus the compressibility and the heat of formation of the crystal from the ions have been given erroneous values. These are corrected.

CHEMICAL ABSTRACTS.

**Activity-coefficient of Normal Potassium Chloride Solution and the Potential of the Normal Calomel Electrode.** JAMES A. BEATTIE (*J. Amer. Chem. Soc.*, 1920, 42, 1128—1131).—The *E.M.F.* of the cell  $\text{Ag, AgCl} | \text{KCl}, N | \text{KHg}_x | \text{KCl} 0.1N | \text{AgCl, Ag}$  has been measured at  $25^{\circ}$ , and the value  $-0.10655$  (mean) obtained. Using this value, the activity ratio of *N*-potassium chloride to *N*/10-potassium chloride is found to be 0.7956. Using this value, the potential of the normal calomel electrode is  $E = -0.2700 + 0.5915 \log 0.592 \times 1.0328 = -0.2826$  volt, a value which is in agreement with that of Lewis, Sebastian, and Brighton (A., 1918, ii, 25). The transport number of potassium in potassium chloride does not change much with dilution; the following values are obtained from the present work and that of MacInnes and Parker (A., 1915, ii, 510): ( $1.0N-0.1N$ ), 0.496; ( $0.5N-0.05N$ ), 0.498; ( $0.1N-0.01N$ ), 0.496; and ( $0.05N-0.005N$ ), 0.494. J. F. S.

**Electrical Conductivity of Pure Salts in the Solid and Fused States. Determination of the Activity-coefficients of Ions in Solid Salts.** JNANENDRA CHANDRA GHOSH (T., 1920, 117, 823—830).

**Free Energy of Dilution and the Transport Numbers of Lithium Chloride Solutions.** DUNCAN A. MACINNES and JAMES A. BEATTIE (*J. Amer. Chem. Soc.*, 1920, 42, 1117—1128).—The *E.M.F.* of cells of the type  $\text{Ag, AgCl} | \text{LiCl}(c_1) | \text{Li(Hg)}_x | \text{LiCl}(c_2) | \text{AgCl, Ag}$ , without a liquid junction, has been measured

at 25° for cells in which  $c_1$  and  $c_2$  varied between 3.0*N* and 0.001*N*, and a further series of *E.M.F.* measurements has been obtained for cells with liquid junctions of the type  $\text{Ag, AgCl} | \text{LiCl}(c_1) || \text{LiCl}(c_2) | \text{AgCl, Ag}$ . From the measurements, the activities of the ions and the degree of ionisation of lithium chloride have been calculated. The following values of  $\alpha$  have been obtained: 0.001*N*, 0.976; 0.003*N*, 0.962; 0.01*N*, 0.932; 0.03*N*, 0.899; 0.1*N*, 0.834; 0.3*N*, 0.759; 1.0*N*, 0.641; and 3.0*N*, 0.458. By combining the two sets of *E.M.F.* values, the transport numbers of the ions have been calculated, and, where possible, the values have been compared with the best values obtained by the Hittorf method. Since these numbers change rapidly with the concentration, a method has been devised by which the numbers can be calculated from the *E.M.F.* values and expressed as a function of the ion activity. In this way, the value of the transport number at any given concentration can be obtained. The following transport numbers of lithium in lithium chloride are obtained: 0.001*N*, 0.359; 0.005*N*, 0.341; 0.01*N*, 0.334; 0.02*N*, 0.327; 0.05*N*, 0.318; 0.10*N*, 0.311; 0.20*N*, 0.304; 0.30*N*, 0.299; 0.50*N*, 0.293; 1.0*N*, 0.286; 2.0*N*, 0.276; and 3.0*N*, 0.268.

J. F. S.

### Electrochemical Behaviour of the Sulphates of Thallium.

G. GRUBE and A. HERMANN (*Zeitsch. Elektrochem.*, 1920, **26**, 291—297. Compare Abegg and Spencer, A., 1905, ii, 369).—The influence of the current density, acidity, and the anode material on the anodic formation of thallic sulphate in sulphuric acid solution has been investigated. It is shown that low current densities and a high acid concentration increase the current yield, and that a specific action of the anode material is active in the formation. The oxidation potential  $\text{Tl}^+/\text{Tl}^{+++}$  in sulphuric acid solution has been re-measured, and the normal potential found to be  $\epsilon_h = +1.211$  volts. This value is independent of the acidity and the total concentration over a wide range. The difference between the value of Abegg and Spencer (*loc. cit.*),  $\epsilon_h = +1.156$ , and the present value is probably due to the liquid junction potential not being entirely accounted for in the earlier work. The potential obtained indicates that it is not possible to oxidise thallous sulphate to thallic sulphate in acid solution to a measurable extent by means of oxygen, and, for the same reason, thallous sulphate is unusable as a reaction accelerator of the oxygen electrode in an oxygen-hydrogen electrode with sulphuric acid as electrolyte. The potential of completely oxidised thallic sulphate solutions lies above that of the reversible oxygen potential. Consequently, it was possible to show that in such solutions, the potential of which was  $\epsilon_h = +1.26$  volts, the bubbling through of oxygen converted some of the thallic sulphate into thallous sulphate. This spontaneous reduction was accelerated by light and platinised platinum.

J. F. S.

**The Critical State of Ethyl Ether.** AUDANT (*Compt. rend.*, 1920, **170**, 1573—1575).—Using an optical method for studying

the critical opalescence and the variation of the critical temperature with the density of filling the tubes, the author obtains for ethyl ether the equation  $T_c = 190.22^\circ + 11D - 10D^2$ , where  $D$  is the density of filling. With rising temperature, opalescence commences  $0.5^\circ$  below  $T_c$  and finishes  $2.5^\circ$  above it, the same limits defining opalescence during cooling. The temperature of maximum opalescence is greater than  $T_c$ , and is higher the greater is the density of filling. The intensity of opalescence also increases with the density of filling.

W. G.

**Equation of State.** FRED. G. EDWARDS (*Chem. News*, 1920, **121**, 3).—A theoretical paper in which equations are given for various quantities. It is stated that the molecular heat equation  $k = m^x \log T$  may be converted into the equation of state,  $b(k + a \log \theta) = m^x \log T$ , where  $\theta$  is the number of degrees below the critical temperature,  $a$  an infinitesimal coefficient producing the relative values of the intrinsic pressures at the critical and observational temperatures, respectively, and  $b$  is a constant making the sum in brackets equal to the intrinsic pressure, the surface tension, or the volume density with any given units. The values of  $y$  obtained from  $m = 5.95/y$  and  $m = 4 - (2y/2.95)$  will give the specific heats at variable volume, whilst  $m$  will be integral at the natural temperature of change of phase and recalcence. The specific density ratio,  $D = A m^x \log T$ ; the coefficient of linear expansion,  $d.V/3d.T = 1/3d.1/A m^x \log T = T/3A m^x$ . The atomic volume ratio,  $V = 1/m^x \log T$  is a more general form of the equation of Lothar Meyer's curve,  $V = A/D$ .

J. F. S.

**Molecular Heat Equation.** FRED. G. EDWARDS (*Chem. News*, 1920, **120**, 277—278).—A theoretical paper in which the author discusses the formula  $y = f(\log T - \log \theta)$ , in which  $\theta$  is the temperature at which  $y$  is one half the constant 5.95. The expression gives the relation between the entropies of different substances (Lewis and Gibson, A., 1918, ii, 29).

J. F. S.

**Entropy of Gases.** RICHARD C. TOLMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 1185—1193).—Making use of his theory of similitude (*Physical Rev.*, 1914, **3**, 244; **4**, 145; 1915, **6**, 219; 1916, **8**, 8; 1917, **9**, 237), the author has deduced the expression  $S = 3/2R \log_e m + 5/2R \log_e T - R \log_e p + S_0$  as a general equation for giving the entropy of a gas,  $S_0 = 3/2R \log_e a$ , and is a general constant independent of the gas. For constant temperature ( $298^\circ$  abs.) and constant pressure, the equation becomes  $S_{298} = 6.87 \log m + c$ , where  $c = 25.1$ . The entropy of mercury, cadmium, zinc, platinum, molybdenum, tungsten, helium, argon, hydrogen ( $H_2$ ), bromine, iodine, and hydrogen (H) has been calculated by the above equation for  $25^\circ$  and 1 atm. pressure, and the values compared with the experimental values of Lewis and Gibson (A., 1918, ii, 29), and it is shown that where wide extrapolation is not necessary there is very good agreement between the calculated and experimental values. The least agreement is found in the

cases of molybdenum and tungsten, where extrapolation has to be made over  $1700^{\circ}$  and  $2100^{\circ}$  respectively; on the other hand, it is to be noted that in the case of platinum, where extrapolation extends over  $1500^{\circ}$ , there is a rather better agreement between the two values than in the case of hydrogen, where no extrapolation is necessary. J. F. S.

**Modified Form of Freezing-point Apparatus.** O. MAASS (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 97—99).—To prevent supercooling, a crystal of solid solvent is produced in the solution by the following device. A short piece of platinum wire is sealed through the tube at the side so as to be in contact with the solution. This projects outside the tube into a side-arm in the air jacket, the opening of which passes outside the cooling-bath through a side-neck. When supercooling begins, a small copper cylinder cooled in solid carbon dioxide is introduced through the side-arm and brought in contact with the platinum wire for a short time. A crystal forms on the tip of the wire in the solution. When the freezing point is determined a second time, it is possible to limit the supercooling to one-tenth of a degree. J. R. P.

**Latent Heats of Vaporisation of Methane and Ethane.** JOHN SATTERLY and JOHN PATTERSON (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 123—127).—Two methods were used. In the first, an electrically-heated wire evaporated some of the liquid, and in the second, a piece of copper was lowered into the liquid. In both cases, the evaporated hydrocarbon was collected over water. The heat supplied was calculated from the watts expended in the first case and the heat capacity of the copper in the second. The results (which are approximate) were: methane, 130 cal. per gram; ethane, 260 cal. per gram J. R. P.

**Heat of Sublimation and Valence Forces of Carbon Modifications.** K. FAJANS (*Zeitsch. Physik*, 1920, **1**, 101—118. Compare this vol., ii, 354).—The heat of combustion of any aliphatic compound may be resolved into the following effects:  $nx$ , where  $x$  is the effect of breaking up of the union C-H and  $n$  is the number of such unions broken;  $nv$ ,  $v$  being the effect of the sub-reaction  $H + \frac{1}{4}O_2 = \frac{1}{2}H_2O$  and  $n$ , as before, the number of such sub-reactions;  $ny$ , where  $y$  is the heat effect of splitting the union C-C and  $n$  as before; and  $nz$ , where  $z$  is the effect of the reaction  $C + O_2 = CO_2$ ,  $n$  as before. From a consideration of the heats of combustion, it is shown that the energy needed to break the single bond group C-C in a saturated hydrocarbon is the same as the energy needed to break up the same group in diamond, where all the atoms are the same distance apart and, therefore, held to each other with the same valence power. This energy is shown to have a value equal to one-half the heat of sublimation of diamond. This value of the heat of sublimation is calculated in two ways: (1) by the equation of Grüneisen; (2) from a consideration of the

change of temperature of the electric arc with the pressure, this temperature being the sublimation temperature of carbon. From the data of Lummer, the heat of sublimation is calculated with the aid of the Clapeyron equation. This value is corrected to that of the heat of sublimation of diamond. The value of the quantity  $y$  as given above may then be calculated, and the value of  $z$  is obtained from the equation  $z + 2y = C$ , where  $C$  is the heat of combustion of diamond. The value of  $v$  is calculated from yet other considerations, and the quantity  $x$  is then obtained from the equation  $-nx + nv - ny + nz = K = \text{heat of combustion of some aliphatic compound}$ . The values of these heat effects are as follows:  $x = -115,000$  cal.,  $y = -143,000$  cal.,  $v = 74,000$  cal.,  $z = 381,000$  cal. From these values, the heat of combustion of any aliphatic compound, for example, ethane, can be computed, thus:  $-(6 \times 115,000) + (6 \times 74,000) - 143,000 + (2 \times 381,000) = 373,000$  cal. The heat effects of splitting the groups  $C=C$  and  $C \equiv C$  can also be calculated. All values given are for  $20^\circ$ . It is also pointed out that, in spite of the difference in the arrangement of the atoms in diamond, graphite, and amorphous carbon, the total energy of the interatomic forces is within 1 or 2% of the same value.

CHEMICAL ABSTRACTS.

**Heat of Formation of Water.** W. A. ROTH (*Zeitsch. Elektrochem.*, 1920, **26**, 288—291).—A theoretical paper in which the various experimental data on the heat of formation of water are critically discussed, and, as a result, modified data are obtained, which are used to recalculate the heat of formation. The results obtained are: heat of formation from hydrogen and oxygen at  $18^\circ$  and under constant pressure is  $68.38$ ,  $15^\circ$  Cal., and at  $0^\circ$  the heat of formation of ice is  $69.96$ ,  $15^\circ$  Cal. The heat of fusion of ice per gram is  $79.67$ ,  $15^\circ$  Cal., and the molecular lowering of the freezing point is  $1.860^\circ$ .

J. F. S.

**Restatement and Correction of the Thermochemical Data on Organic Compounds. I. The Data of P. V. Zubov.** W. SWIENTOSLAWSKI (*J. Amer. Chem. Soc.*, 1920, **42**, 1092—1100).—In a previous publication (A., 1918, ii, 32), the author advocates the use of naphthalene with a heat of combustion of  $9612$ ,  $15^\circ$  Cal., as a standard for determining the heat capacity of calorimetric bombs. In the present paper, the author has recalculated the whole of the thermochemical data of P. V. Zubov, obtained at Warsaw between 1892 and 1910 (compare A., 1899, i, 589; 1902, ii, 188; 1904, ii, 159, 382; 1907, ii, 230; 1913, ii, 385, 830). The results for forty hydrocarbons, forty-one alcohols, twenty-three ketones, seven esters, nine acids, and six nitrogen compounds are given in tables, which include the heat of combustion of 1 gram of the substance weighed in air, the molecular heat of combustion ( $p$  or  $v$  const.), the molecular heat of the substance weighed in a vacuum, and the heats of combustion of the substances in the gaseous condition at constant pressure.

J. F. S.

**Heat of Adsorption of Vapours on Charcoal.** ARTHUR B. LAMB and A. SPRAGUE COOLIDGE (*J. Amer. Chem. Soc.*, 1920, **42**, 1146—1170).—The heat of adsorption by charcoal of the vapours of carbon tetrachloride, diethyl ether, chloroform, ethyl formate, carbon disulphide, methyl alcohol, ethyl chloride, ethyl bromide, ethyl iodide, benzene, and ethyl alcohol has been determined at 0° over a considerable range. The resulting values are shown to be reproducible and independent of the rate of adsorption of the vapour and of the previous history of the charcoal. The heat of adsorption in all cases can be represented very precisely as a function of the amount adsorbed by the expression  $h = mx^n$ , where  $h$  is the heat of adsorption per normal c.c. of vapour,  $x$  the number of c.c. of vapour adsorbed, and  $m$  and  $n$  constants which are characteristic of the vapour. The constant  $n$  is found to be very nearly unity. The heat of adsorption, therefore, decreases but slightly with increasing amount of adsorption. In other words, there is but slight evidence of fatigue in the adsorptive forces. It has been shown that this decrease, represented by  $1 - n$ , is antitab to the boiling points of the liquids; that is, the liquids with relatively high boiling points exhibit a small value for  $1 - n$ , and hence a slight fatigue. This is due to the fact that such liquids have a high latent heat of vaporisation. The constant  $m$  also varies relatively little from vapour to vapour. In general,  $m$  and  $n$  tend to vary in opposite directions. In agreement with this, the actual molecular heats of adsorption of the various liquids measured are not very different, varying between 12.0 cal. for ethyl chloride and 15.5 cal. for carbon tetrachloride. The heats of adsorption of these vapours are very nearly the same on inactive as on active charcoal of the same kind. Vapours containing halogens appear to react with the charcoal when warmed, so as to decrease the heat developed by any subsequent adsorption of gas, without, however, greatly affecting the fatigue effect. The net heats of adsorption, that is, the heats developed above those corresponding with the latent heats of vaporisation, are approximately of the same magnitude as the latent heats of vaporisation, and the net heats of adsorption per c.c. of liquid are very nearly identical for all the liquids studied. The net heats of adsorption are closely proportional to the heats of compression under high pressure. This indicates that the liquids are all attracted by the charcoal with substantially the same force, and that the net heat of adsorption is merely a heat of compression. The absolute value of this attractive force appears to be about 37,000 atmospheres where 1 c.c. of liquid is adsorbed on 10 grams of charcoal. The molecular adsorbability, that is, the number of c.c. of gas adsorbed at a fixed gas pressure (20 mm.), is inversely proportional to the molecular volume of the liquid. The molecular adsorbability is inversely proportional to the net molecular heat of adsorption. This regularity follows from the previously mentioned regularities. All the above evidence indicates that the liquid films studied are at least one, and usually very many molecules thick, and this is



confirmed by a consideration of the actual volume occupied by the liquid and the approximately known capillary volume and surface of the charcoal.

J. F. S.

**"Vapour Density" a Misnomer.** PHILIP BLACKMAN (*Chem. News*, 1920, **120**, 292).—The author maintains that the term vapour density is incorrect for the quantities usually called by this name; these are in reality vapour specific gravities. The term vapour density should be used for the weight of unit volume of a gas or vapour under standard conditions.

J. F. S.

**Variation of the Coefficient of Viscosity of Gases with Temperature.** ROBERT CLARK (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 177—180).—If two vessels of known volumes be connected by a capillary tube, any pressure difference between them will gradually disappear, owing to flow through the capillary. This flow can be calculated in terms of the rate of change of pressure difference and the volumes of the two vessels; from the dimensions of the capillary tube, the coefficient of viscosity may be determined. If the rate of change of pressure be observed when the apparatus is maintained at different temperatures, the values of the coefficient of viscosity corresponding with these temperatures may be obtained. The viscosities of carbon dioxide, hydrogen, and dry air at temperatures between 0° and 110° were determined, and the value of the coefficient  $n$  in the equation  $\mu = \mu_0(T/273.1)^n$  found to be: air, 0.750; carbon dioxide, 0.965; hydrogen, 0.700. The viscosity of air at 23.0° was found to be  $184.0 \times 10^{-6}$ .

J. R. P.

**The Effect of the Addition of certain Fatty Acids on the Interfacial Tension between B.P. Paraffin Oil and Mercury.** SHANTI SWARUPA BHATNAGAR and WILLIAM EDWARD GARNER (*J. Soc. Chem. Ind.*, 1920, **39**, 185—187*t*. Compare Wells and Southcombe, *ibid.*, 51*t*).—The measurements of interfacial tension between the oil and mercury were made by the dropping pipette method, as described by Donnan (*A.*, 1900, ii, 201). The four acids used were oleic, stearic, linolic, and palmitic acids, and curves are given showing the surface tensions of solutions of varying concentrations of these acids in B.P. paraffin oil. The curve for oleic acid shows a point of inflexion at a concentration of about 0.25%. The curves for oleic, stearic, and palmitic acids are very similar in character, especially at the higher concentrations, but the surface tensions of the linolic acid solutions are much lower than those of the corresponding solutions of the other three acids. The curves obtained are very similar to those given by Langmuir for fatty acids (*A.*, 1917, ii, 525), and, applying Langmuir's views, it would appear that the increased efficiency as a lubricant of a mineral oil to which an organic acid is added runs parallel with a lowering of tension at the metal-oil interface.

W. G.

**Density of Adsorbing Materials.** STUART McLEAN (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 197—199).—The density of

materials was found by the volumenometer method, using helium as the filling gas, since it is not adsorbed at ordinary temperature. The following mean results were found: coconut charcoal (heated to  $400^{\circ}$ ), 1.53; lignite carbonised at  $350^{\circ}$ , 1.33; lignite carbonised at  $450^{\circ}$ , 1.46; lignite carbonised at  $550^{\circ}$ , 1.44. J. R. P.

**Properties of Wood Charcoal.** ALWYN PICKLES (*Chem. News*, 1920, 120, 301—302).—It is shown that coconut charcoal, prepared by heating at  $900^{\circ}$ , becomes more efficient towards a gas on keeping for some time in the air; this may be due to sorption of water, but it is also due to a spontaneous disintegration of the charcoal. Prolonged heating increases the efficiency of the charcoal, and treatment with acid removes sulphur as hydrogen sulphide and prevents friability. Birch charcoal is a more efficient absorber of colouring matter than animal charcoal, and since its density (1.46) is about one half that of animal charcoal, mechanical stirring is not required to the same extent. The adsorption of water from solutions of alkali haloids (negative adsorption) has been investigated at various temperatures. It is shown that at  $40^{\circ}$  the negative adsorption suddenly increases, and it is at this temperature that the interior of the charcoal is becoming opened out by the solvent action of the solution. It is very probable that the first removal of the water from the solution is due to the surface effect of the charcoal (true adsorption) and that as the temperature rises this effect diminishes with the decreasing surface tension of the water. The interior, or absorption, effect, however, continues to increase and speedily more than counterbalances the decreasing surface effect.

The following types of substances are negatively adsorbed from aqueous solutions: (i) those of simple structure; (ii) highly ionised substances; (iii) compounds with a strongly electropositive cation; (iv) compounds with a univalent metallic cation; (v) compounds having ions with a high mobility. J. F. S.

**Effect of Pressure on Gas Adsorption.** ALWYN PICKLES (*Chem. News*, 1920, 121, 1—2).—Equal volumes of charcoal (50 c.c.) from birch chips, coconut, fruit-stone dust, palm nut, almond, and birch dust were rendered free from air by heating and saturated with ammonia at ordinary pressure and temperature. They were then placed individually in an air-tight glass vessel fitted with a manometer and an aspirator tube, and the pressure reduced to a measured point. The apparatus was closed and the change of pressure with time observed. The initial pressures were about 20, 40, and 60 cm. In all cases the pressure at first increased, and eventually (one to two hours) decreased, but in no case was the initial pressure regained. The first effect of aspiration is to remove the gas on the charcoal surface, then gas escapes from the interior, and so increases the pressure, the subsequent decrease being due to surface condensation. The results give an indication of the inner structure of the charcoal. Where a rapid increase of pressure occurred, a complex internal structure may be

assumed (coconut and fruit-stone charcoal). In the case of birch dust, the gas-adsorbing capacity is mainly a surface effect. Palm-nut charcoal was used in large pieces, and it retained the gas mainly by absorption. The apparent density,  $AD$ , and the true density,  $D$ , have been determined for each variety used, and the following values obtained: almond,  $AD$  0.48,  $D$  1.70; birch chips,  $AD$  0.23,  $D$  1.44; fruit stone,  $AD$  0.68,  $D$  1.72; birch dust,  $AD$  0.21,  $D$  1.47; coconut,  $AD$  0.63,  $D$  1.71; and palm nut,  $AD$  0.64,  $D$  1.59. The carbon content of all varieties was about 85%. The porosity of charcoal dust is increased by mixing it with solid ammonium dichromate and heating out of contact with air. In this way, the gas-absorbing efficiency per c.c. of actual charcoal is increased, but per c.c. of the whole product it is decreased. As gas adsorbents, the denser charcoals are the most efficient; the order of efficiency is palm nut, coconut, fruit stone. J. F. S.

**Adsorption of Gases by Carbonised Lignites.** STUART McLEAN (*Trans. Roy. Soc. Canada*, 1919, 13, iii, 187—199).—The adsorption of air, carbon dioxide, oxygen, hydrogen, and nitrogen by lignite was studied. Oxygen is adsorbed much more readily than nitrogen. The presence of water vapour decreases the amount of gas adsorbed. No permanent adsorption takes place, since there are but few cases where the last weight is greater than the first, and these may be due to experimental error. Chemical action may be taking place in the case of oxygen. The fact that in most cases the last weight is less than the first indicates that the oxygen combines with the lignite, forming carbon dioxide, which is given off when the lignite is heated, making the sample lighter.

J. R. P.

**Velocity of Sorption.** ALWYN PICKLES (*Chem. News*, 1920, 121, 25—27).—The sorption by charcoal of benzoic acid from alcohol solution at 14°, iodine from  $N/10$ -potassium iodide solution at 15°, 25°, 50°, and 70°, and potassium permanganate in  $N/10$ -concentration from water at 12°, 25°, 50°, and 70°, has been determined with respect to the velocity with which these substances are taken up. It is shown that, on applying the equation for unimolecular reactions to these cases, a "constant" is obtained which continually decreases, but by using the equations

$$K = 1/t \{ \log_e a/(a-x) - 0.4343x/a \}$$

and  $K = 1/(t_2 - t_1) \{ \log_e (a-x_1)/(a-x_2) - 0.4343(x_2-x_1)/a \}$  a very fair constant is obtained in the case of iodine and benzoic acid, whilst very irregular values are obtained for permanganate. These are attributed to catalytic decomposition of the permanganate by the charcoal, solvent action of the solution in opening up the charcoal capillaries, and the reducing effect of the charcoal. In all the above cases birch-dust charcoal was used.

The velocity of sorption of ammonia and hydrogen chloride by coconut charcoal has been determined at 13°. In the case of ammonia, the "constant" of the unimolecular equation falls steadily with time, but the equations mentioned above give a good

constant. With hydrogen chloride, the "constant" of the unimolecular reaction gives a moderately good constant, but the value of  $K$  increases rapidly with time, which seems to show that the hydrogen chloride is continually opening up fresh surfaces.

J. F. S.

### **The Absorption of Colouring Matters by Charcoal.**

EDMUND KNECHT (*J. Soc. Dyers and Col.*, 1920, **36**, 201).—Knecht replies to the statement by Philip, Dunnill, and Workman (*T.*, 1920, **117**, 302) that Knecht and Hibbert (*J. Soc. Dyers and Col.*, 1916, **32**, 226) correlate the activity of a charcoal in decolorising solution with its nitrogen content, and shows their original contention to be that whilst for a basic dye, such as methylene-blue, the nitrogen content does not affect the absorptive power, for an acid colour, such as crystal-scarlet, the absorptive power of an animal charcoal is in proportion to its fixed nitrogen content. This contention has not yet been controverted. Knecht still regards the absorption of methylene-blue as being connected with the oxygen content of the charcoal.

A. J. H.

### **The Deliquescence and Drying of Ammonium and Alkali Nitrates and a Theory of the Absorption of Water Vapour by Mixed Salts.**

E. B. R. PRIDEAUX (*J. Soc. Chem. Ind.*, 1920, **39**, 182—185T).—The author has measured the vapour pressures of saturated solutions of ammonium nitrate, potassium nitrate, and of a solution saturated with ammonium nitrate and sodium nitrate. The results of the latter determinations show the added difficulty of drying an impure salt, and also, if such has to be dried, that raising the temperature is not necessarily and in all cases advantageous. If the ratio, relative humidity of salt to relative humidity of air, is greater than 1, drying is possible, and the speed of drying could probably be expressed by the van't Hoff maximum work expression,  $4.57T \log p_1/p$  for 18 grams of water, where  $p_1$  is the pressure of water vapour in the atmosphere and  $p$  is the pressure of water vapour in equilibrium with the univariant system, salt-saturated solution-vapour, at a given temperature.

The gains in weight of sodium nitrate plus varying amounts of sodium chloride in atmospheres of different humidities have been measured. The manner in which deliquescence occurs in a mixture of soluble salts is discussed, and it is considered that such deliquescence takes place in two stages.

W. G.

### **The Adsorption Capacity of Cellulose. Remarks about the Electrometrical Micro-analysis of Chlorine.**

P. RONA and L. MICHAELIS (*Biochem. Zeitsch.*, 1920, **103**, 19—30).—Cellulose does not appreciably adsorb surface-active non-electrolytes. Only in the case of extremely surface-active substances can very slight adsorption be established. The more marked adsorption of dyes by cellulose is due to the ash content of the cellulose.

The estimation of chlorine by the electrical method with a calomel electrode is described and discussed.

S. S. Z.

**The Condition of Dissociation of Ampholytes. I. The Influence of Univalent Ions Disregarding all Colloidal Phenomena.** L. MICHAELIS (*Biochem. Zeitsch.*, 1920, 103, 225—243).—A theoretical discussion of the influence of ions on the dissociation of acids, bases, and ampholytes, for which they have a chemical affinity.  
S. S. Z.

**Process of Diffusion Through a Rubber Membrane.** H. A. DAYNES (*Proc. Roy. Soc.*, 1920, [A], 97, 286—307).—The diffusion of hydrogen, nitrogen, oxygen, carbon dioxide, nitrous oxide, and ammonia through rubber sheets has been examined by means of the katharometer (this vol., ii, 503). It is shown that the behaviour of a set of rubber films agrees in all respects, within the limit of the experiments, with that predicted from assumptions of a simple process of diffusion through a rubber membrane. The conclusion previously reached, that the surface resistance is negligible, is thus confirmed. The method furnishes a rapid and satisfactory means of measuring the absorption and the diffusion constant of a material for a gas, and is capable of a high degree of precision. The mean value of the diffusion constant for the three films examined was  $11.4 \times 10^{-6}$  cm./sec. at  $20^{\circ}$ , the actual values being  $11.7 \times 10^{-6}$ ,  $10.4 \times 10^{-6}$ , and  $13.6 \times 10^{-6}$  cm./sec. The mean value of the absorption coefficient was 0.035 at normal pressure and  $20^{\circ}$ , the actual values being 0.035, 0.037, and 0.031. The coefficient of absorption has a low temperature-coefficient, approximately 0.5%/1°, compared with that of the diffusion constant. It is not that which is responsible for the great variation of permeability with temperature. This suggests that the process of absorption is a simple molecular action.  
J. F. S.

**The Cause of the Influence of Ions on the Rate of Diffusion of Water Through Collodion Membranes. II.** JACQUES LOEB (*J. gen. Physiol.*, 1920, 2, 563—576).—The effect of ions carrying charges of different signs on the free osmosis of water through a collodion membrane which separates it from a solution of an electrolyte has been discussed previously (compare this vol., ii, 94, 233, 234). It is now shown that the influence of the concentration of electrolytes on the rate of transport of water through collodion membranes in electrical endosmosis is similar to that in the case of free osmosis.

On the basis of Helmholtz's theory of electrical double layers, this influence of an electrolyte on the rate of diffusion of water through a collodion membrane is due to the ions increasing or decreasing the density of charge on the membrane. The relative influence of the oppositely charged ions on this density is not the same in all concentrations. The influence of the ion with the same sign of charge increases in the lowest concentrations more rapidly with increasing concentration than the influence of the ion with the opposite sign of charge, whilst for somewhat higher concentrations the reverse is true.  
W. G.

**The Reversal of the Sign of the Charge of Membranes by Hydrogen Ions.** JACQUES LOEB (*J. gen. Physiol.*, 1920, 2, 577—594).—When a collodion membrane is treated with a protein, the membrane assumes a positive charge when the hydrogen-ion concentration of the solution with which it is in contact exceeds a certain limit (compare preceding abstract). By this treatment, a thin film of protein adheres to the membrane, and the positive charge of the membrane is localised in this protein film. The hydrogen-ion concentration at which the reversal in the sign of the charge of a collodion membrane treated with a protein occurs varies in the same sense as the isoelectric point of the protein with which the membrane has been treated, and is always slightly higher than that of the isoelectric point of the protein used. Thus the critical hydrogen-ion concentration required for the reversal appears to be that concentration where enough of the protein lining of the membrane is converted into a protein-acid salt, for example, gelatin nitrate, capable of ionising into a positive protein ion and the anion of the acid used. W. G.

**Atomic Structure and Crystal Symmetry.** HANS THIRRING (*Physikal. Zeitsch.*, 1920, 21, 281—288).—A theoretical paper in which the symmetry of crystals, particularly that of the diamond and sylvine, is considered. Since the reflexion of Röntgen rays from the lattice surface of a crystal depends only on the number of electrons per unit surface, and is independent of the orientation of the atoms, account must be taken of the possibility that the length of edge of the elementary cube of the atom lattice is an integral multiple of that of the corresponding point lattice. This multiple is represented by  $n$ , and, taking account of this possibility, the following points are deduced: The carbon atom cannot possess a cylindrical symmetry, that is, it has not a Bohr single-plane system of electrons. Systems with crossed electron rings cannot be brought into line with the symmetry of the diamond; on the other hand, those systems to which Landé attributes a tetrahedral symmetry may be brought into line with the diamond symmetry. The explanation given by Bragg ("X-Rays and Crystal Structure," p. 158) for the hemihedrism of potassium chloride, namely, that the atoms do not occupy exactly the corners of the cube or the middle points of the surfaces, but positions a little removed from them, must be abandoned, because this explanation leads to the value  $n=2$ , which does not agree with any equilibrium position. It is not possible to construct a regular enantiomorphic symmetry for potassium chloride from axial symmetric atoms so long as the assumption is maintained that no potassium or chlorine atom is different from the others. Using Landé's atom model, the hemihedrism of potassium chloride can be explained by  $n \geq 2$  if it is assumed that the magnetic forces set up by the potassium atom play an important part in the properties of the symmetry of the crystal. From the holohedrism of sodium chloride, it follows that the magnetic forces of the alkali metals decrease down the periodic system group in the sense that

they are unnoticeable in the case of sodium, but in the case of potassium they exercise an influence on the crystal symmetry.

J. F. S.

**Crystallisation of Supersaturated Solutions and Supercooled Liquids.** D. McINTOSH (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 265—272).—The sizes of particles of solid which induce crystallisation of supersaturated sodium sulphate solution and supercooled salol were found to be: sodium sulphate,  $10^{-13}$  to  $10^{-16}$  gram in one method,  $10^{-12}$  to  $10^{-14}$  gram in another; salol,  $10^{-9}$  gram to  $4 \times 10^{-15}$  gram. These are much below the numbers formerly accepted.

J. R. P.

**Periodic Precipitation. I. Silver Chromate in Gelatin.**

ALEXANDER MITCHELL WILLIAMS and MARY RUSSELL MACKENZIE (*T.*, 1920, **117**, 844—852).

**Composition of the Vapour and Liquid Phases of the System Methane-Nitrogen.** H. A. McTAGGART and E. EDWARDS (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 57—66).—The temperature-composition diagram for the system methane-nitrogen at atmospheric pressure was obtained, and the constants in the formula  $\log r' = a + b \log r$ , where  $r$  = ratio methane/nitrogen in liquid, and  $r'$  the corresponding ratio in the vapour, determined as  $a = -0.47$ ,  $b = +0.85$ .

J. R. P.

**Velocity of Reactions.** M. POLANYI (*Zeitsch. Elektrochem.*, 1920, **26**, 228—231).—A theoretical paper in which certain difficulties in the deduction of the equations for the velocities of reactions are discussed (compare Herzfeld, A., 1919, ii, 503; Polanyi, this vol., ii, 238).

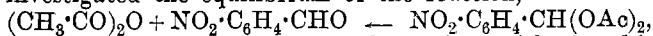
J. F. S.

**Reaction Isochore and Velocity of Reaction from the Statistical Point of View.** M. POLANYI (*Zeitsch. Elektrochem.*, 1920, **26**, 231).—A correction of some of the mathematical expressions in a previous paper (this vol., ii, 238).

J. F. S.

**The Ignition of Gases. I. Ignition by the Impulsive Electrical Discharge. Mixtures of Methane and Air.** RICHARD VERNON WHEELER (*T.*, 1920, **117**, 903—917).

**Colloidal Solutions and Organic Syntheses. II. Mechanism of the Synthesis of Nitrobenzylidene Diacetate.** M. BAKUNIN and F. GIORDANI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1917, [iii], **23**, 39—50. Compare A., 1916, ii, 421).—The authors have investigated the equilibrium of the reaction,



both without solvent and in ethereal solution, with the object of deducing the heat of the reaction by means of van't Hoff's equation,  $d \log K / dT = -Q / RT^2$ .

The results of the experiments with *p*-nitrobenzaldehyde and

acetic anhydride in ethereal solution, and in presence of ferric oxide or phosphoric oxide, show that these oxides merely alter the velocity with which the condition of equilibrium is reached, the reaction being thus catalytic.

The reactions without solvent were carried out in presence of a colloidal solution of phosphoric oxide in acetic anhydride; here, too, the results show that this condensing agent acts purely catalytically. The value of  $Q$  is 3.911 cal. and 9.247 cal. for the reactions with *o*- and *p*-nitrobenzaldehyde respectively. With the meta-compound, the solubility in acetic anhydride is very slight at low temperatures, and the values of the reaction constant obtained at higher temperatures are of about the same order of magnitude as the experimental error.

The probable mechanism of the action of colloidal solutions in these reactions is discussed (compare Duclaux, A., 1911, ii, 479; de Hemptinne, A., 1904, ii, 224; Burton, A., 1906, ii, 275; Perrin, A., 1905, ii, 138).

T. H. P.

**The Catalytic Decomposition of Hydrogen Peroxide by Colloidal Platinum.** A. DE GREGORIO ROCASOLANO (*Compt. rend.*, 1920, 170, 1502—1504).—Contrary to the conclusion of Bredig, it is shown that when electrosols of platinum are used, the decomposition of hydrogen peroxide by colloidal platinum is not a unimolecular reaction. During the reaction, the catalyst itself apparently undergoes some change. This altered catalyst will decompose further quantities of the peroxide, and the reaction is then unimolecular.

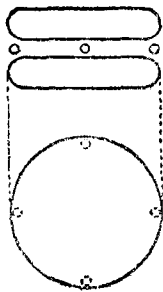
W. G.

**Annual Report of the International Committee on Atomic Weights for 1920–1921** (T., 1920, 117, 885—888).

**The Nuclei of Atoms and the New Periodic System.** WILLIAM D. HARKINS (*Physical Rev.*, 1920, 15, 73—94).—A summary and extension of previous papers on the nuclear structure of atoms. The data on which any theory of nuclear structure are based are atomic masses, atomic numbers which are assumed to be equal to nuclear charges, and atomic stabilities (given by the periods of disintegration when the atoms are radioactive), supposed by the author to be related to the relative abundance of the atomic species (elements) in nature. From these data, it is assumed (1) that all nuclei consist of positive electrons (or hydrogen nuclei  $=\eta^+$ ) or eta particles, and negative electrons ( $\beta^-$ ). Almost all of these are grouped in  $\alpha^{++}$  particles or helium nuclei  $=\eta_4^+\beta_2^-$ ; a few are grouped as mu particles ( $\mu=\eta_2^+\beta_2^-$ ), both of which carry an even net charge; and a few as nu particles [ $\nu=(\eta_3^+\beta_2^-)^+$ ], which have an odd charge, and are responsible for the existence of most atoms of odd atomic number, which are relatively rare. Thus, negative electrons almost always occur in pairs as binding electrons in these primary groups. Also pairs of cementing electrons are present in all heavy nuclei where they are



used to attach extra  $\alpha$ -particles. Only the cementing electrons are given off in the disintegration of radio-atoms. The atomic weights indicate that chlorine, silicon, magnesium, neon, copper, zinc, nickel, and all elements with numbers from 28 to 80 (Hg), consist of mixtures of isotopes. All atomic weights of atomic species are approximately whole numbers, with the exception of hydrogen, which has the weight 1.0078. These whole numbers are given by the Harkins-Wilson equation,  $W = 2(N + n) + \frac{1}{2} + \frac{1}{2}(-1)^{N-1}$ , where  $n$  is the number of cementing electrons in the nucleus, and varies in steps of 2 up to 26, which is the maximum. Using this equation, Durrant showed the normal plot for the cementing electron content of atoms. A simpler equation is  $W = 2(N + n)$ . Equations are also given for the number of  $\alpha$ -particles and cementing electrons in the nucleus. The atomic weight of the  $\alpha$ -particle in complex nuclei is 4.000, as nearly as can now be told. If any atomic weights, except that of hydrogen, are not integers, it is only the atomic weights of the radioactive elements which deviate, and these may possibly be slightly higher than the corresponding whole numbers. The  $\alpha$ -particle is assumed to consist of four positive electrons at the corners of a square lying in a plane, with one negative binding electron above and one below the plane.



The negative electrons are, with Rutherford, assumed to be relatively large, so that each one is close to all four positive electrons. This structure (see fig.) is assumed to be responsible for the difference in weight between the positive electrons and the  $\alpha$ -particle. Nearly all elements are mixtures, so the term "atomic species" is proposed to indicate all atoms of one composition and structure. It is only the atomic weights of the atomic species which are whole numbers, since most of the mixtures (elements) are not in the proper proportion to give this result. An element may have an integer for an atomic weight if (1) it

consists of one species, or (2) when only one isotope has a sufficient stability to make it evident in the atomic weights. The former is probably the case with such light atoms as oxygen, whilst the latter is true of the radioactive elements. Between atomic numbers 82 and 10 (possibly below this), is the region of stable isotopes. Two classes of isomeric atoms exist. (1) Non-isotopic isomerides, as  $UX_1$ ,  $UX_2$ , and  $U_2$ , or  $\alpha_{58}\mu\beta_{26}e'_{86}e_4$ ,  $\alpha_{58}\mu\beta_{25}e'_{86}e_5$ , and  $\alpha_{58}\mu\beta_{24}e'_{86}e_6$ , and (2) isotopic isomerides, which have the same nuclear composition. Here  $e$  represents a valence, and  $e'$  a non-valence planetary electron. Of the ordinary atoms, calcium and argon are isomeric, the difference in structure being due to the inclusion of two cementing electrons in the argon nucleus, which in calcium are present in the planetary system of non-nuclear electrons. The formulæ for the composition of the first twenty-seven elements and the radioactive elements are given, and it is possible to express radioactive changes by equations. Thus,  $\alpha_{59}\mu\beta_{26}e'_{86}e_6$  is the

formula for uranium,  $\alpha_{58}\beta_{26}e'_{86}e_4$  for thorium,  $\alpha_{51}\mu\beta_{20}e'_{78}e_4$  for radio-lead, and  $\alpha_{52}\beta_{22}e'_{78}e_4$  for thorium-lead. An alpha change is then indicated by the equation  $\alpha_{58}\beta_{26}e'_{86}e_4 \rightarrow \alpha_{57}\beta_{26}e'_{86}e_2 + \alpha^{++} + 2e^-$  (Th to meso-Th'), whilst a beta change is of the type  $\alpha_{58}\mu\beta_{23}e'_{78}e_5 + e^- \rightarrow \alpha_{53}\mu\beta_{22}e'_{78}e_6 + \beta^-$  (Ra-C to Ra-C'). In the nuclear structure of the light elements, the  $\nu$ -group ( $\eta_3\beta_2$ ) occurs frequently, and is characteristic of the odd-numbered elements. Experiments proving that chlorine is a mixture of isotopes are nearing completion. These consist in a separation of chlorine into a lighter and a heavier fraction by diffusion.

## CHEMICAL ABSTRACTS.

**Electrons and Chemical Potential.** FRED G. EDWARDS (*Chem. News*, 1920, **120**, 292—293).—A discussion of some points put forward by Henri (*Etudes de Photochimie*, Gauthier-Villars, Paris). The author derives the following statements from Henri's work. (1) Given the true graphic formula of any compound, the single bond represents one electron between the respective atoms. (2) The double bond appears when this single electron is withdrawn. The characteristic vibration is displaced towards the infra-red by the consequent increase of mass in the vibrator, changing the speed of propagation and consequently the angle of dispersion. The three double bonds usually shown for benzene do not exist. (3) A triple bond appears when a second electron is similarly removed from the same pair of atoms. (4) A complete wave-length of incident light reciprocating with one electron of a molecule constitutes reciprocal absorption and emission. (5) An infra-red half-wave-length ( $E=h\nu$ ) absorbed by a molecule represents the addition of one electron. (6) An ultra-violet half-wave-length ( $E_1=h\nu_1$ ) absorbed represents the motion of an electron the distance of half a wave-length from one position in the molecule to another, and provides the mechanism of tautomerism. (7) There is a similar number of ultra-violet bands, the respective frequency of which is a large integral multiple of every respective infra-red band, the latter representing the total removal or replacement of an electron, but the former merely a rearrangement of its position in the molecule.

J. F. S.

**An Electronic Theory of Isomerism.** W. E. GARNER (*Nature*, 1920, **104**, 661—662).—The theory differentiates between two kinds of valency, according as the rotation of the electrons with respect to the valency is clockwise or anti-clockwise. Various types of isomerism (for example, eight possible isomerides of cinnamic acid) are discussed on the basis of this theory. All the isomerides, except the optical pairs, should possess different free energies, according to the arrangement of the rotating electrons.

J. R. P.

**Space Filling and Ionic Mobility.** RICHARD LORENZ (*Zeitsch. Elektrochem.*, 1920, **26**, 221—228).—A theoretical paper, in which

the relationships between the filling of space by the molecules and the ionic mobility are discussed. It is shown from these relationships that the mobility may be calculated within limits from the space filling. This calculation is based on Stokes's formula applied to large ions, and it gives values for the molecular radii which are of the correct order of magnitude. The molecular volume of the ions obtained in this way is compared with the molecular volume of the ion substance, and in the majority of cases it is found that the molecular volume of the ions ( $\phi$ ) is smaller than the molecular volume of the ion substance ( $V_0$ ). The term space-filling ( $\psi$ ) is defined as the ratio of the space occupied by the molecules to that occupied by the mass of substance, and for the purpose of obtaining comparable results the last-named quantity is referred to absolute zero. The ratio is expressed by  $\psi = \phi/V_0$ . The space-filling figures can be calculated from the different theories of the equations of condition. The results are tabulated. Since the equations of condition are not absolutely definite, the space-filling is obtained as a value between two extremes,  $0.74 > \psi > 0.25$ . The space-filling values calculated from the ionic mobility all lie between these two extremes. A table of values is given which includes those for sixty univalent organic cations, thirty-seven univalent organic anions, six bivalent organic cations, and thirteen complex inorganic salts. This relationship constitutes electroconductivity as a branch of experimental atomistics. The experimental space-filling values correspond approximately with the space-filling in cubic packing. The equations of condition of Sutherland and Reinganum correspond most closely with the requirements of the present work. The  $\psi$ -curves obtained are shown to represent a first approximation only. Ions with normal space-filling numbers cannot be hydrated.

J. F. S.

**Theory of Electrolytic Ions. XV. Space-filling and the Mobility of Univalent Organic Anions.** RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1920, **111**, 148—150. Compare A., 1919, ii, 212, 262, 264; this vol., ii, 410).—The univalent organic anions bear a different relationship between the space filling and the mobility than do the cations (*loc. cit.*). The volume of the ion substance ( $V_0$ ) is analogous to that in the case of the cations;  $V_0 = \sigma \times z$ , where  $\sigma$  is the stere (5.75) and  $z$  is the number of atoms in the ion. The molecular volume of the ion  $\phi$ , and the volume of the ion substance  $V_0$ , give the space-filling numbers  $\psi$ , according to the equation  $\phi/V_0 = \psi$ .

J. F. S.

**Structure of Matter and the Quantum Theory.** F. H. LORING (*Chem. News*, 1920, **120**, 291; **121**, 2—3).—Supplementary notes to the author's previous paper (this vol., ii, 365). The table previously given is completed up to, and including, nickel.

J. F. S.

**Experiments with a New Micro-balance.** HANS PETTERSSON (*Proc. Physical Soc.*, 1920, **32**, 209—221).—The balance is wholly

of quartz, the usual knife-edge support being replaced by a pair of quartz fibres. Magnetic arrestment is employed, and balance obtained by displacement of a bulb at different pressures of air or magnetically. The range of weighings depends on the size of the beam; with one 5 cm. in length, the maximum load is 100—200 mg., and the setting can be made to within  $10^{-7}$  mg.

J. R. P.

**Use of Acetylene as a Source of Heat in Chemical Laboratories.** NAUMANN (*Zeitsch. angew. Chem.*, 1920, **33**, i, 148).—Acetylene is readily generated from calcium carbide, and when burnt in a specially constructed Bunsen burner yields a very hot, non-luminous flame.

W. P. S.

**Explosion Accident at the Chemical Institute, University of Munster i.W., and Its Cause.** R. SCHENCK (*Zeitsch. angew. Chem.*, 1920, **33**, ii, 245; *Chem. Zeit.*, 1920, **44**, 497).—During a lecture experiment to show combustion by combined oxygen, in which a mixture of toluene and tetranitromethane was being burnt, a violent explosion occurred, by which some thirty people were more or less injured. The cause of the explosion lay in the faulty preparation of the mixture. The correct quantities for safe burning are 67.5 c.c. of tetranitromethane (D 1.65) and 7.5 c.c. of toluene (D 0.8), but in place of this 67.5 grams of tetranitromethane and 7.5 grams of toluene had been taken, that is, the relative proportion of toluene was doubled.

J. F. S.

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### Inorganic Chemistry.

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**Reaction between Hydrogen Peroxide and Peracids. A.**  
Rius y MIRÓ (*Anal. Fis. Quim.*, 1920, 18, 35—42).—It is shown that hydrogen peroxide, previously proposed as a reagent for hydroperoxides (this vol., ii, 368), reduces peracids of the types  $\text{RO}_2\text{R}$  and  $\text{RO}_2\text{H}$ . The author repeated the experiments of Riesenfeld (A., 1905, ii, 825; 1909, i, 963; ii, 951; 1910, ii, 51), according to whom perchromic acid has the formula  $\text{H}_3\text{CrO}_8$ ; but, instead of 5 mols. of oxygen evolved per mol. of dichromate (thus,  $2\text{CrO}_8''' + 12\text{H}' = 2\text{Cr}''' + 6\text{H}_2\text{O} + 5\text{O}_2$ ), he found 4.6 to 6.5, which he explains by assuming the formation of Caro's acid. The author did not measure the evolved oxygen, but determined the amount of undecomposed hydrogen peroxide with permanganate, after adding the dichromate through a burette to the mechanically agitated acid solution of hydrogen peroxide. The oxygen evolved was found to be 3.71 to 4.33 mols. per mol. of dichromate. The greater evolution of oxygen corresponded with a low acidity,

because peracids are hydrolysed in acid solutions. The highest values must be due to the formation of an unstable higher perchromic acid. The ethereal solution of perchromic acid is gradually decomposed by hydrogen peroxide. Permonophosphoric, pervanadic, and perbenzoic acids are also acted on by hydrogen peroxide.

W. R. S.

**Preparation of Hydrogen Chloride from Chlorine and Water.** H. D. GIBBS (*J. Ind. Eng. Chem.*, 1920, 12, 538—541.)—By a reversal of the Deacon process, hydrogen chloride may be produced from chlorine and water with the employment of charcoal as a catalyst. The speed of the reaction is governed by the temperature, the relative concentrations of water and chlorine, and the character of the charcoal. For temperatures of 0°, 12°, 25°, and 37·5°, with a charcoal layer of 10 cm. depth and 10·75 sq. cm. cross-section, weight 67 grams, and mesh 8 to 10 per in.; a gas velocity of 500 cm. per min.; air-chlorine ratio, 500:1; water content of air, 50% saturation; pressure of gas above charcoal, 1 atm., and below, 1 atm. less 0·85 cm. water, the curves of production, after the initial rise, gradually flatten. Under the same conditions, but at a temperature of 25°, with water content of 0, 20, 40, and 80% saturation, and ratios of water to chlorine of 0:1, 3:1, 6·2:1, and 12·4:1, the curves indicate that the production of hydrogen chloride in each case reaches a constant rate dependent on the amount of water present. With two varieties of charcoal, a maximum hydrogen chloride production of 34%, falling off to 18% after 800 mins., and of 26%, falling to 7%, was obtained.

W. J. W.

**The Chemical Nature of Sulphur Chloride [Sulphur Dichloride].** MAX BERGMANN and IGNAZ BLOCH (*Ber.*, 1920, 53, [B], 977—979).—The preparation of the trisulphides of benzoic and anisic acids in 70—90% yield by the action of sulphur chloride on the potassium salts of the necessary thio-acid (this vol., i, 548) is of peculiar interest, since the chloride behaves as a definite chemical substance,  $\text{SCl}_2$ . The individuality of the compound has, however, been frequently doubted, and it has been regarded as a solution of chlorine or of chlorine and sulphur tetrachloride in sulphur chloride. Were this the case, the action of potassium thiobenzoate on it should yield a mixture of benzoyl di- and tetrasulphides, which might possibly be mistaken analytically for the trisulphide. Examination of molar mixtures of the compounds, however, shows that their physical behaviour is quite unlike that of benzoyl trisulphide, so that there is no possibility of confusion. The experiments therefore confirm the individuality of the chloride, which has previously been shown to be probable by determinations of molecular weight.

H. W.

**Production and Utilisation of Sulphur Dichloride.** (Sir) WILLIAM JACKSON POPE and CHARLES THOMAS HEYCOCK (*Brit. Pat.* 142879).—The employment of 1% by weight of finely

powdered absorbent charcoal as a catalyst greatly facilitates the reaction between chlorine and sulphur monochloride, and similarly, when sulphur dichloride is subjected to conditions which lead to its decomposition into chlorine and the monochloride, recombination is facilitated by similar means. G. F. M.

**Arsenic-free Sulphuric Acid.** K. SCHERINGA (*Pharm. Weekblad*, 1920, 57, 421—422).—The greater part of the arsenic may be removed by heating the acid, after the addition of a little sulphite, so that some vapour is given off continuously. The acid is then diluted with an equal volume of water and electrolysed for at least one day. W. S. M.

**Absorption of Nitrogen Oxides by Dilute Nitric Acid.** ERIC K. RIDEAL (*J. Ind. Eng. Chem.*, 1920, 12, 531—538).—The absorption of nitrogen dioxide by dilute nitric acid in presence of air was investigated with 10, 5, and 1%  $\text{NO}_2$ -air mixtures with nitric acid containing 50, 25, 10, and 8%  $\text{HNO}_3$  at temperatures of 30°, 40°, and 50°, and the results are plotted on curves. Absorption in strong nitric acid proceeds most rapidly at low temperatures, but with water the reverse occurs. The point of inversion, that is, where absorption is independent of temperature, is reached with approximately 10% nitric acid. The limitation of the nitric acid concentration to 64% in absorption towers is caused by reduction of nitric acid by the nitrogen trioxide produced. The equilibrium constant of  $2\text{HNO}_3 + \text{N}_2\text{O}_3 \rightleftharpoons \text{H}_2\text{O} + \text{N}_2\text{O}_4$  at ordinary temperatures is  $K=0.81$ . By agitation with oxygen, the  $\text{N}_2\text{O}_3$  is converted into  $\text{NO}_2$ , and a higher strength of nitric acid is obtained, and by cooling a 12%  $\text{NO}_2$ -air mixture to 20° to remove excess of water above that required for the equation  $2\text{N}_2\text{O}_4 + 2\text{H}_2\text{O} + \text{O}_2 = 3\text{HNO}_3$ , and then refrigerating to -10°, nitric acid of 61.2—78.1%  $\text{HNO}_3$  was produced. W. J. W.

**Pressure Measurements of Corrosive Gases. The Vapour Pressure of Nitrogen Pentoxide.** FARRINGTON DANIELS and ARTHUR C. BRIGHT (*J. Amer. Chem. Soc.*, 1920, 42, 1131—1141).—An apparatus is described whereby the pressure of corrosive gases may be measured to a fraction of a millimetre. The essential part of the apparatus is a glass diaphragm, 1 cm. diameter and 0.1—0.2 mm. thick, made by flattening the bottom of a small bulb. The flat place and a short length of the stem are thickly coated with platinum, a glass arm with a rounded end, also platinised, is fused to the tube a short distance below the platinum coat, and bent twice at right angles, so that the rounded end just touches the flattened diaphragm, thus making an electrical contact between them. The arm and diaphragm are connected by means of platinum wires with a low-voltage cell and a galvanometer. The diaphragm is mounted in the apparatus containing the corrosive gas, so that the underside comes in contact with the gas, whilst the top is in contact with a variable air

pressure, which can be measured. Changes of pressure deflect the diaphragm and break the circuit, so that it is comparatively simple to see when the pressure of the gas under investigation is exactly balanced by a measured air pressure. This manometer has been used to determine the vapour pressure of nitrogen pentoxide at temperatures  $243.0-305.5^{\circ}$  abs. Nitrogen pentoxide was prepared by placing 25 c.c. of 100% nitric acid in a glass-stoppered wash-bottle and mixing with small quantities of phosphorus pentoxide until a thick paste was obtained. The mixture was kept in ice and salt during the mixing. The bottle was then connected with a U-tube containing phosphoric oxide, a second empty U-tube immersed in ice and salt to collect the pentoxide, and a protecting U-tube of phosphoric oxide. The mixture was warmed to  $35-40^{\circ}$ , and the system of tubes subjected to intermittent exhaustion. In this way, 5-10 grams of crude nitrogen pentoxide were condensed in two hours. The nitrogen pentoxide was purified by sublimation in a current of dry ozonised air, and condensed as a colourless, crystalline mass in the experimental tubes. All measurements of vapour pressure were made in the dark, and, since nitrogen pentoxide rapidly decomposes in the gaseous state, an estimation of the rate of decomposition was made at each temperature, and the vapour pressure corrected for this. The vapour pressure of nitrogen pentoxide is represented by the empirical formula  $\log P_{mm} = 1244/T + 34.1 \log T - 85.929$ , which is more in keeping with the experimental results than the formula of Russ and Pokorny (*Monatsh.*, 1913, **34**, 1027). The experimentally determined values are closely in agreement with those of Russ and Pokorny. The following values were obtained:  $258^{\circ}$  abs., 13 mm.;  $263^{\circ}$  abs., 21 mm.;  $268^{\circ}$  abs., 32 mm.;  $273^{\circ}$  abs., 51 mm.;  $278^{\circ}$  abs., 79 mm.;  $283^{\circ}$  abs., 118 mm.;  $288^{\circ}$  abs., 183 mm.;  $293^{\circ}$  abs., 279 mm.;  $298^{\circ}$  abs., 420 mm.;  $303^{\circ}$  abs., 620 mm.;  $305.5^{\circ}$  abs., 760 mm. The heat of sublimation has been calculated for various temperatures; the following values are obtained for various absolute temperatures:  $263^{\circ}$ , 12,360 cal.;  $268^{\circ}$ , 12,640;  $273^{\circ}$ , 12,760;  $278^{\circ}$ , 13,110;  $283^{\circ}$ , 13,360;  $288^{\circ}$ , 14,160;  $293^{\circ}$ , 14,140;  $298^{\circ}$ , 14,040.

J. F. S.

**The Transition from Coal to Coke.** ERIC SINKINSON (*T.* 1920, **117**, 839-843).

**The Oxidation of Coals.** MARCEL GODCHOT (*Compt. rend.*, 1920, **171**, 32-34).—The coal used was divided into two fractions by extraction with pyridine. The original coal gained 3.15% by weight by oxidation in one month at  $100^{\circ}$ . The extract and the residue after extraction only gained, under similar conditions, 1.22% and 1.99% respectively, whereas when the coal was reconstructed by mixing extract and residue together, this mixture gained 3.20%. The theory of bacterial action in the oxidation of coal is scarcely in accord with these results, as any such bacteria would have been destroyed during the extraction with pyridine.

W. G.



**The Electromotive Activity of Carbon Monoxide. III.**

K. A. HOFMANN (*Ber.*, 1920, **53**, [B], 914—921. Compare A., 1916, ii, 637; 1919, ii, 23).—The present communication deals with the reactions involved in the oxidation of carbon monoxide at copper surfaces moistened with alkali.

It is found that carbon monoxide is slowly oxidised in open circuit, the electrolyte ultimately containing, in addition to carbonate, traces of formate and scarcely any oxalate; the monoxide is gradually replaced by hydrogen, so that the reaction proceeds according to the scheme:  $\text{CO} + 2\text{KOH} = \text{K}_2\text{CO}_3 + \text{H}_2$ . In the closed circuit, the hydrogen is oxidised to water by oxygen liberated at the opposite electrode. Copper cannot, however, bring gaseous molecular hydrogen into a condition of electromotive activity, but can be very actively charged by nascent hydrogen, most simply by cathodic polarisation.

It appears probable that carbon monoxide, owing to the existence of subsidiary valencies, has the power to unite with alkali hydroxide in the presence of copper to yield small amounts of an isoformate,  $\text{Cu} \dots \text{C}(\text{OH})(\text{OK})$ , which then combines with a further molecule of the hydroxide to yield the alkali carbonate, whilst the hydrogen is liberated in the atomic state at the copper. This conception is supported by the observation that active elements are not formed from copper, carbon monoxide, and water, or from carbon monoxide and alkali hydroxide alone, but only from copper, alkali hydroxide, and carbon monoxide in conjunction. It is further found that hydrated cupric oxide is only reduced by carbon monoxide in the presence of alkali at an appreciable rate if a certain amount of metallic copper is present. Again, the electromotive activity of carbon monoxide at a copper; and to a less degree at a platinum, surface is not immediately developed, whilst, in the absence of hydroxyl ions, carbon monoxide is not noticeably activated by copper. Cuprous oxide does not play a part in the phenomena, since it is found that hydrated cupric oxide is directly reduced in the presence of alkali to the metal, whilst the presence of a minute amount of oxygen diminishes the electromotive force of the system  $\text{Cu}-\text{CO}-\text{alkali}$  in a striking, if transitory, manner.

H. W.

**Revision of the Atomic Weight of Silicon. Analysis of Silicon Tetrachloride.** GREGORY P. BAXTER, PHILIP F. WEATHERILL, and EDWARD O. HOLMES, jun. (*J. Amer. Chem. Soc.*, 1920, **42**, 1194—1197).—The atomic weight of silicon has been determined from the analysis of silicon tetrachloride. The tetrachloride was prepared by the action of chlorine on silicon, filtered to remove ferric chloride, and then kept in contact with mercury for a week in an exhausted flask to remove excess of chlorine. The clear liquid was then carefully fractionated at low temperatures by the method previously described by Baxter and Starkweather for tin tetrachloride (this vol., ii, 436), and sealed into a series of small bulbs. The more volatile portions, which probably contain hydrogen chloride, and the less volatile portions,

which probably contain silicon hexachloride, titanium tetrachloride, and carbon tetrachloride, were rejected. The bulb was weighed and broken under a solution of chloride-free sodium hydroxide, the solution was acidified with nitric acid and precipitated with about the correct amount of pure silver nitrate solution of known concentration, and the end-point determined by means of a nephelometer. As a mean of four experiments, the ratio  $\text{SiCl}_4:4\text{Ag}=0.393815$ , whence the atomic weight of silicon is 28.111 ( $\text{Cl}=35.457$ ,  $\text{Ag}=107.880$ ).

J. F. S.

**Helium: its Production and Uses. A Lecture Delivered before the Chemical Society on June 17th, 1920.** JOHN CUNNINGHAM MCLENNAN (T., 1920, 117, 923—947).

**Helium in Brannerite.** ROGER C. WELLS (*J. Franklin Inst.*, 1920, 189, 779—780; *Chem. News*, 1920, 121, 22).—The gas liberated when brannerite (this vol., ii, 257) is fused with hydrogen sodium sulphate was found, spectroscopically, to contain helium.

L. J. S.

**Continuous Flow Apparatus for the Purification of Impure Helium Mixtures.** E. EDWARDS and R. T. ELWORTHY (*Trans. Roy. Soc. Canada*, 1919, 13, [iii], 47—52).—Helium containing at least 12% of impurity can readily be purified by passing it in a continuous stream over charcoal at the temperature of liquid air or oxygen. The rate of flow can be increased to at least 10 litres per hour without decreasing the efficiency of the process. The maximum rate of flow was not determined. By the use of two or more sets of charcoal tubes in parallel, the process may be made continuous, as the charcoal may be revived without disturbing the flow.

J. R. P.

**Combustibility of Mixtures of Hydrogen and Helium.** JOHN SATTERLY and E. F. BURTON (*Trans. Roy. Soc. Canada*, 1919, 13, [iii], 211—215).—The combustibility was tested by a lighted match and by a white-hot platinum spiral. Under the conditions of experiment, the percentage of hydrogen could be raised to 26 before the mixture became inflammable; if the percentage exceeded 28, the mixture would burn.

J. R. P.

**Formation and Decomposition of Sodium Hypochlorite.** F. GIORDANI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1919, [iii], 25, 138—153).—Investigation of the action of chlorine on solutions of sodium hydroxide under different conditions shows that the primary action consists in the formation of sodium hypochlorite, and is followed by decomposition of the latter, with formation of chlorate and chloride and liberation of oxygen. The distribution between these two reactions of the active chlorine, which disappears, depends notably on the illumination, the temperature, the concentration of free sodium hydroxide, and the nature of the vessel, and possibly on other factors.

The formation of hypochlorite is accompanied by increase in volume, which must be taken into account in calculating the amount of sodium hydroxide required to yield hypochlorite of definite titre.

The concentration of the free sodium hydroxide in the product exerts a marked influence on the stability. Contrary to Lunge's interpretation ("Sulphuric Acid and Alkali," Vol. III, 1911), of Cotellet and Descosses' results (*Mon. Sci.*, 1903, 624), perfectly neutral sodium hypochlorite solution is not stable, but undergoes rapid decomposition. In practice, the action is best arrested when the solution contains 1.5% of sodium hydroxide.

The statement that the law, according to which the percentage decomposition of the hypochlorite per unit time varies with the concentration, is not in agreement with theoretical considerations is erroneous.

T. H. P.

**The Arsenites of Lithium and Potassium.** F. A. H. SCHREINEMAKERS and (MLLE) W. C. DE BAAT (*Rec. trav. chim.*, 1920, **39**, 423—428).—A study of the ternary system, lithium oxide—arsenious oxide—water, at 25° shows the existence of one arsenite  $\text{LiAsO}_2$ , which is soluble in water without decomposition. A similar study shows that potassium gives two arsenites,  $\text{K}_2\text{As}_4\text{O}_7$  and  $\text{K}_6\text{As}_4\text{O}_9 \cdot 12\text{H}_2\text{O}$ , both of which are soluble in water without decomposition.

W. G.

**Crystal Structure of Cæsium Dichloro-iodide.** RALPH W. G. WYCKOFF (*J. Amer. Chem. Soc.*, 1920, **42**, 1100—1116).—Cæsium dichloro-iodide has been stated to crystallise in two forms, rhombic and hexagonal (rhombohedral). The rhombohedral form is obtained by dissolving 10 grams of cæsium chloride in 50 c.c. of water, adding 8 grams of iodine, and passing chlorine through the hot solution until the iodine has dissolved. On cooling slowly, six-sided plates, about 1 cm. diam. and less than 1 mm. thick, are formed. All attempts to prepare the rhombic variety failed. When the method recommended by Wells and Penfield (*A.*, 1892, 773) was used, crystals were obtained which appeared to be rhombic, but, when examined by the X-rays, the pattern indicated that they were twinned, and on breaking the crystals, they were frequently found to be hollow. The density of the rhombohedral form is found to be 3.86. The structure of the crystals was obtained from the X-ray spectrum obtained from the anticathode of an X-ray bulb, using the crystal as a grating, and from a study of the Laue patterns obtained by passing X-rays through a section of the crystal. It is shown that the body centred unit rhombohedron contains one molecule. The cæsium atom is placed either at the centre or the corner of this unit, and the iodine atom either at the corner or the centre. Two chlorine atoms lie on the long diagonal very close to 0.31 of its length from the corners. Because of the supposedly very nearly equal scattering power of cæsium and iodine, it is impossible at present to decide between the two possibilities.

J. F. S.

**Additive Compounds of Ammonia with Ammonium Haloids.** JAMES KENDALL and J. G. DAVIDSON (*J. Amer. Chem. Soc.*, 1920, **42**, 1141—1145).—The freezing-point curves of the ammonium haloids with ammonia have been determined over the whole available composition range. It is shown that in the case of ammonium fluoride, no compounds are formed, and that this substance is practically insoluble in liquid ammonia. In the other cases, the following compounds are shown to exist,  $\text{NH}_4\text{Cl}, 3\text{NH}_3$ , m. p.  $10.7^\circ$ ;  $\text{NH}_4\text{Br}, 3\text{NH}_3$ , m. p.  $13.7^\circ$ ;  $\text{NH}_4\text{I}, 3\text{NH}_3$ , m. p.  $-8.0^\circ$ ; and  $\text{NH}_4\text{I}, 4\text{NH}_3$ , m. p.  $-5.1^\circ$ . Other compounds of these systems previously recorded were not observed, and in all probability do not exist. The stability of the additive compounds with ammonia increases regularly as the series of the ammonium haloids is ascended, and it is therefore held to be likely that some of these compounds may be capable of existence in the vapour phase.

J. F. S.

**Some Reactions started by a Primer.** ERNEST BERGER (*Compt. rend.*, 1920, **170**, 1492—1494).—Numerous reactions, when started by localised heating, will spread throughout the whole mass. The priming mixture suggested by the author consists of sixty parts of potassium nitrate or sodium nitrate and forty parts of industrial calcium silicide. This mixture can be lit with a match, and its combustion produces a very high temperature. It has been used to start such reactions as the reduction of boron phosphate or arsenate by aluminium, the reduction of calcium or barium sulphate by red phosphorus, the preparation of silicon and boron fluorides from lead fluoride.

W. G.

**Production of Chlorides by Primed Reactions.** ERNEST BERGER (*Compt. rend.*, 1920, **171**, 29—32. Compare preceding abstract).—Aluminium will replace a number of metals and metalloids from their chlorides by spontaneous action or by a primed reaction. In some cases, magnesium is still more active. In the same way, a considerable number of metals, such as calcium, magnesium, aluminium, manganese, etc., will displace the carbon from organic chlorides, such as carbon tetrachloride, tetra- and hexa-chloroethane, and chloroform. Such actions, when started, continue with the generation of a considerable amount of heat, the metallic chloride being vaporised. In the case of liquid organic chlorides, these may first be absorbed in kieselguhr or sawdust. Such mixtures found application in the production of smoke clouds during the war.

W. G.

**Complex Salt Formation.** E. H. RIESENFELD and H. FELD (*Zeitsch. Elektrochem.*, 1920, **26**, 286—288).—A solution of barium sulphate in 90% sulphuric acid has been electrolysed between platinum electrodes by a current of 190 milliamperes and 440 volts. After the current had passed for seven and a-half hours, the change in concentration in the anode and cathode cells was determined.

The results show that the barium migrates to the anode as a complex ion, and that in consequence the compound usually termed barium hydrogen sulphate must be regarded as a complex acid of the formula  $H_2[Ba(SO_4)_2]$ . Similar experiments were carried out with a solution of silver chloride in 35% hydrochloric acid, and it was found that here also a complex acid of the formula  $H[AgCl_2]$  is present.

J. F. S.

**Experimental Determination of the Vapour Pressure Curves of Molten Cadmium and Zinc, and the Calculation of the Chemical Constants of Cadmium, Zinc and Monatomic Bromine.** H. BRAUNE (*Zeitsch. anorg. Chem.*, 1920, **111**, 109—147).—The vapour pressure of molten cadmium and zinc has been determined for small pressures (up to 79 mm.) by the circulation method, and for pressures up to 2 atms. by the boiling-point method. The results are represented by the equations,  $\log p = -5763/T - 1.28 \log T + 12.282$  for cadmium, and  $\log p = -6655/T - 1.147 \log T + 12.046$  for zinc. The specific heats of the molten metals have been determined over a considerable range of temperature. The atomic heats calculated from the specific heats are practically constant over the temperature range between the melting point and the boiling point. The values found are: cadmium 7.50, zinc 7.24. The chemical constant of both elements was calculated from the vapour-pressure measurements, and the values  $1.54 \pm 0.2$  for cadmium and  $1.11 \pm 0.7$  for zinc obtained, which are in keeping with theory for the chemical constants of monatomic gases. The chemical constant of monatomic bromine has been determined from Bodenstein's measurements of the dissociation of bromine (A., 1916, ii, 552). The calculation could not be strictly carried out because of lack of information on the specific heat of bromine at low temperatures; nevertheless, the values obtained are shown not to be at variance with the theory of the chemical constants of monatomic gases.

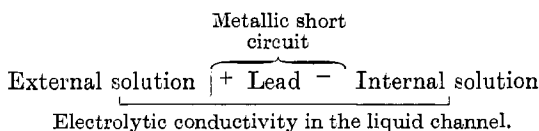
J. F. S.

**The Transmutation of Simple Substances.** LAURENT NAUDIN (*Mon. Sci.*, 1920, [v], **10**, 121—122).—A very brief account of unpublished experiments of Schützenberger, in which he found that, when lead, carefully purified from silver, was chlorinated by chlorine gas and subsequently reduced by hydrogen at a high temperature, the lead then contained traces of silver. This process was repeated several times on the same sample of lead, carefully purified between each process, always with the same results.

W. G.

**Formation of the Autogenous Lead-tree.** A. THIEL (*Ber.*, 1920, **53**, [B], 1066—1072).—It has been shown by Senderens that a lead-tree is formed when the metal is immersed in solutions of certain lead salts, and the phenomenon has been explained by Cohen and Helderman (A., 1915, ii, 456) on the basis of the presumed allotropic forms of lead. Since the author has shown, how-

ever, that lead does not form allotropes (following abstract), this explanation is no longer tenable. Crystallographical examination of autogenous and other lead-trees, of electrolytic lead, and of solidified lead shows the crystals to be invariably of the same type and to be composed of combinations of octahedron and cube. The formation of the autogenous tree occurs uniformly under acidified solutions of lead nitrate, but very seldom (in two cases out of fifty) under Heller's solution. The explanation is to be found in the author's theory of desglomeration (following abstract). Local ionic concentration systems are set up in the interstices between the crystallites as the nitrate solution penetrates into them, and becomes exhausted without the possibility of free admixture with the external, less exhausted solution. There are thus formed short-circuited ionic concentration cells, thus:



in consequence of which the lead-tree becomes developed at irregular positions over the whole surface of the metal. With Heller's solution, the tendency towards the formation of such cells is much less pronounced, since under the most favourable conditions the potential developed does not exceed 10 millivolts, whilst with the nitrate solutions it may even exceed 40 millivolts. H. W.

**The supposed Allotropy of Lead.** A. THIEL (*Ber.*, 1920, 53, [B], 1052—1066).—It has been shown by Heller (*A.*, 1915, ii, 634) that compact lead ultimately crumbles to a powder when preserved beneath acidified solutions of lead salts, and the phenomenon has been attributed to allotropic change. The results, and also the nature of the product, have been confirmed by Cohen and Helder mann (*A.*, 1915, ii, 456), who, however, consider that several allotropes are formed. The author's experiments, on the other hand, lead him to the conclusion that the phenomenon is not due to allotropy, but to simple chemical action.

The majority of the experiments were performed with samples of commercial soft lead containing about 0.005% of iron, and no other impurity in detectable amount. In consequence of the difficulties regarding the supply of gas, they were generally effected at the ordinary temperature, about 18°, although at times the temperature fell as low as 0°. In conformity with Heller's solution (molar with respect to lead acetate and 0.4*N* with respect to nitric acid), the solutions were, in general, molar as regards lead salt and 0.4*N* as regards acid. Strips of lead weighing 8—10 grams, which had previously been repeatedly etched by dilute nitric acid, were immersed in about 10 c.c. of the necessary solutions.

The disintegration of lead is only observed in solutions which

contain nitrate ions, and does not occur, for example, with lead acetate and acetic acid, lead chloride and hydrochloric acid, lead nitrite, lead silicofluoride and hydrofluosilicic acid, lead perchlorate and perchloric acid. Disintegration which has been started in specimens of lead by Heller's solution is arrested when they are transferred to nitrate-free solutions. Lead is slowly attacked when immersed in Heller's solution, nitrogen and nitric oxide being evolved, and the metal being considerably dissolved previous to the commencement of the stage at which it begins to fall to powder. Similarly, the metal is attacked by solution of nitrates which are free from lead; reaction, however, starts more slowly, so that it would appear that the process is catalysed by the presence of lead ions or lead nitrite.

Further evidence against the theory of the formation of an allotrope of lead is afforded by inspection of the disintegrated product, which is found to consist of homogeneous, irregularly polyhedral granules with more or less rounded edges; these are, in general, relatively large in size and free from small crystals, such as would be expected if a new modification had been formed. Again, according to Cohen and Helder mann, the transition temperature lies at about  $50^{\circ}$  ( $60^{\circ}$  according to Jänecke), above which the compact modification is stable; it is found, however, that lead rapidly disintegrates under Heller's or other solution containing nitrate at  $100^{\circ}$ , although unaffected under these conditions in acidified lead acetate and lead perchlorate solutions. Lastly, only a very slight difference of potential is observed between compact and disintegrated lead immersed in lead perchlorate solution.

The author explains the phenomenon in the following manner. Compact lead is composed of crystallites, the crevices of which are filled by a finely granular eutectic, which is present even in "pure" metals (a similar structure must be assumed for all metals which have solidified from the molten state). This eutectic is more readily attacked by a suitable agent when the impurities are more chemically active than the metal itself; in consequence, cavities are formed around the crystallites, which finally become so deep that the latter are completely detached from the main mass. (The term "disglomeration" is proposed for the phenomenon.) In support of this hypothesis, it is shown that disintegration can also be effected by other suitable agents, as, for example, when a lead anode slowly dissolves in a solution of perchloric acid, although the action is less marked in this case. On the other hand, disglomeration is only to be expected when dealing with solidified metals, and it is interesting to note that lead crystals, in the form of the lead-tree, are only resolved into the individual crystals when immersed in hot or cold Heller's solution, whilst, further, massive lead can be protected from disintegration by coating it with a deposit of electrolytic lead. Attempts are also described to find other instances of disglomeration, and it is shown that copper can be disintegrated by immersion in ammoniacal persulphate solution.

H. W.

**The Composition of Ancient Eastern Bronzes.** MASUMI CHIKASHIGE (T., 1920, 117, 917—922).

**Colloidal Cuprous Oxide.** C. PAAL (*Zeitsch. anal. Chem.*, 1920, 59, 166—167).—Referring to a method described by Ruoss (A., 1919, ii, 367) for the preparation of colloidal cuprous oxide, the author points out that the substance has been known for some considerable time (compare A., 1906, ii, 356, 358; 1914, ii, 656).

W. P. S.

**The Precipitation of Mercuric Salts by Hydrogen Sulphide.** PIERRE JOLIBOIS and PIERRE BOUVIER (*Compt. rend.*, 1920, 170, 1497—1498).—Using the apparatus previously described (this vol., ii, 107, 112) to study the action of varying proportions of hydrogen sulphide on mercuric chloride in dilute solution, it is shown that the black precipitate, formed with excess of hydrogen sulphide, has the composition  $\text{HgS}$ , and the white precipitate, formed in the presence of excess of mercuric chloride, has the composition  $2\text{HgS}, \text{HgCl}_2$ . There is no indication of the existence of any other intermediate compound.

W. G.

**Corrosion of Iron.** R. KATTWINKEL (*Zeitsch. angew. Chem.*, 1920, 33, i, 156).—An incrustation which formed in a steam pipe had strong magnetic properties, and consisted almost entirely (99.12%) of magnetic iron oxide,  $\text{Fe}_3\text{O}_4$ .

W. P. S.

**Action of Metallurgical Additions on the Anomaly of the Dilatability of Nickel Steels.** CH. ED. GUILLAUME (*Compt. rend.*, 1920, 170, 1433—1435).—A detailed study of the action of manganese, chromium, and carbon on the dilatability of nickel steels over the range of easily obtainable alloys, and of a series of nickel steels containing 5% of copper. The addition of any of these third constituents diminishes the intensity of the anomaly of dilatability in the region of its minimum value. In the case of manganese, carbon, and copper, within a limited region of nickel content, ternary alloys are obtained which are slightly less dilatable than the binary alloys with the same nickel content.

If the other constituents are well known, the measurement of the dilatability gives a method of fixing the carbon content to within 1 in 10,000.

W. G.

**Values of the Dilatabilities of Nickel Steels.** CH. ED. GUILLAUME (*Compt. rend.*, 1920, 170, 1554—1557. Compare preceding abstract).—Using nickel steels containing 0.4% of manganese and 0.1% of carbon, the true dilatabilities first decrease to a minimum as the nickel content increases, and then increase again. The minimum value of the dilatability,  $\alpha_{20} 1.19 \times 10^{-6}$ , corresponds with a nickel content of 35.6%. Allowing for the coefficients of dilatability of manganese and carbon, it is shown that such an alloy of pure iron and nickel would have a dilatability equal to  $0.2 \times 10^{-6}$ .

W. G.



**Thermal Change of the Elastic Properties of Nickel Steels.**

P. CHEVENARD (*Compt. rend.*, 1920, **170**, 1499—1502).—A study of the anomaly of elasticity of twenty-eight nickel steels containing varying proportions of nickel and only just the amount of manganese indispensable to forging. The method employed was to measure the time and decrement of oscillation of a torsion pendulum constructed with wires of the steels.

The coefficient of variation of the modulus of torsion is characterised, in reversible alloys, by a rapid increase to a maximum, which corresponds with the minimum of dilatability, and then a gradual diminution. For alloys with a stable state in the cold, the results do not indicate any irregularity.

Tempering and hammer hardening diminish the value of the modulus of torsion, which increases, however, with the temperature of annealing, there being a maximum of rapidity between 450° and 550°.

As in the case of the dilatability, the thermo-elastic coefficient is affected by the treatment which the alloy undergoes. Contrary to what happens in the case of the dilatability, however, hammer hardening diminishes the amplitude of the anomaly, whilst tempering increases it.

W. G.

**The Constitution of the Lilac-grey Complex Chromium Sulphate.**

A. RECOURA (*Compt. rend.*, 1920, **170**, 1494—1497).—The lilac-grey chromium sulphate previously described (this vol., ii, 114) consists of one molecule of the green chromium sulphate and two molecules of the normal violet sulphate. When freshly prepared, the  $\text{SO}_4^{''}$  ions corresponding with the green sulphate are masked, whilst the  $\text{SO}_4^{''}$  ions corresponding with the violet salt are precipitable. On keeping, the latter  $\text{SO}_4^{''}$  ions also become masked. The explanation given is that in the freshly-precipitated lilac-grey salt the green sulphate is in its depolymerised state, but, once solid, it rapidly and spontaneously becomes converted into its polymerised form, and in this form is capable of masking the  $\text{SO}_4^{''}$  ions of the violet salt.

W. G.

**Bromination of Antimony in Ethereal Medium.**

A. RAYNAUD (*Bull. Soc. chim.*, 1920, [iv], **27**, 411—414).—When an excess of dry bromine is added to finely powdered antimony in dry ethyl ether and the liquid boiled for three hours, a crystalline compound, having the composition  $\text{SbBr}_5 \cdot \text{OEt}_2$ , is obtained. When freshly prepared, it does not fume in air, but is decomposed by water. The ether is only removed by heating the compound at 55°. When exposed on a porous plate in a bell-jar over sulphuric acid, the compound is, in a few days, converted into antimony tribromide.

W. G.

## Mineralogical Chemistry.

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**Graphite in Japan.** SEIJIRŌ NODA (*Beitr. Min. Japan*, 1915, No. 5, 260—261).—The various modes of occurrence and origin are briefly discussed. The following analyses show that the scaly graphite from crystalline rocks contains more carbon and less volatile matter than the compact graphite from metamorphosed sedimentary rocks (of Palaeozoic and Mesozoic age):

Rock Matrix.	C.	S.	Volatile matter.	H <sub>2</sub> O.	Ash.
Gneiss .....	88.87	trace	1.86	0.53	8.74
Granite .....	58.00	trace	2.22	0.40	39.38
Palaeozoic .....	20.85	0.44	7.40	0.49	71.24
Mesozoic .....	1.36	0.03	6.72	0.42	91.50

L. J. S.

**Tetrahedrite from Besshi Mines, Prov. Iyo, Japan.** KOTOJIRŌ ARAI (*Beitr. Min. Japan*, 1915, No. 5, 267—268).—Analysis by K. ISHII gave:

Cu.	Sb.	As.	Bi.	S.	Fe.	Ag.
33.672	30.538	0.227	0.139	26.789	4.424	0.487
Au.	Mn.	Ni.	Co.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.
0.0005	0.007	0.007	trace	1.052	1.48	0.30
MgO.						
0.66						

Mercury, zinc, lead, and tin are absent.

L. J. S.

**Calcite Deposit from the Senami Hot Spring, Japan.** DENZŌ SATŌ (*Beitr. Min. Japan*, 1915, No. 5, 281—282).—From a boring made in prospecting for oil at this locality, water at a temperature of 100° gushed out to a height of 20 metres, and the oil concession became a spa. A snow-white, crystalline crust is deposited by the water, and the pipe and conduit have frequently to be cleared. The water is clear and colourless, neutral in reaction, and slightly alkaline in taste, D<sup>14</sup> 1.0035. Analysis gave, in grams per litre:

K.	Na.	Ca.	Mg.	Cl.
0.0786	1.3333	0.1323	0.0003	2.1162
SO <sub>4</sub>	H <sub>2</sub> CO <sub>3</sub> .	H <sub>2</sub> SiO <sub>3</sub> .	CO <sub>2</sub> .	Total.
0.2759	0.0632	0.1928	0.1596	4.3522

Analysis I is of the lower layer, with a slight grey tinge, and II of the colourless, transparent upper layer. D 2.72. Rhombohedra of calcite, with curved faces, are present in the drusy portions:

	CaO.	MgO.	MnO.	Fe <sub>2</sub> O <sub>3</sub> +Al <sub>2</sub> O <sub>3</sub> .	SiO <sub>2</sub> .	CO <sub>2</sub> .	H <sub>2</sub> O.	Total.
I ...	55.14	trace	0.35	0.50	0.36	43.25	0.32	99.92
II .	55.57	—	0.29	0.27	0.14	43.65	0.30	100.22

L. J. S.

**Aragonite Cones formed at the Kuriyama Geysers, Prov. Shimotsuke, Japan.** WATARU WATANABE (*Beitr. Min. Japan*, 1915, No. 5, 237—241).—Hot (94°) water, with a sulphurous odour, issuing from rock crevices gave, on analysis by M. KAWAKITA (grams per litre):

NaCl.	HNaCO <sub>3</sub> .	CaCO <sub>3</sub> .	Na <sub>2</sub> SO <sub>4</sub> .	K <sub>2</sub> SO <sub>4</sub> .	MgCO <sub>3</sub> , MnCO <sub>3</sub> , FeCO <sub>3</sub> .
1.1642	0.1241	0.1600	0.1134	0.0531	traces

D<sup>21</sup> 1.02. The water has an alkaline reaction after boiling. The material of the aragonite cones deposited by this water gave, on analysis by Y. ŌSHIMA:

CaCO <sub>3</sub> .	SrCO <sub>3</sub> .	BaCO <sub>3</sub> .	MnCO <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> +Al <sub>2</sub> O <sub>3</sub> .	Insol.*	Total.
93.26	0.65	0.50	0.99	1.32	3.12	99.84

\* Consisting chiefly of free sulphur and some organic matter.

The interior of the cones consists of calcite, and the central channel through which the water passes is lined with pink crystals of mangano-calcite. A cone, measuring 30 cm. across the base, 30 cm. high, and weighing 13.878 kilos., was formed around an orifice during a period of ten months; and when it was broken off, another cone grew in its place. Some extinct geyser cones at another district in Japan reach a height of 4 metres; these are now transformed into calcite. The hot springs deposit volatile sulphides, such as orpiment, realgar, and cinnabar. L. J. S.

**Calcareous Deposit from Hot Spring Water at Hokuto, Formosa.** KOTORA JIMBŌ (*Beitr. Min. Japan*, 1915, No. 5, 283).—In reservoirs of the hot water, calcium carbonate is deposited as minute, irregular, disk-shaped aggregates of very fine acicular crystals. The deposit is brown in colour, and gave, on analysis by SAEGI:

CaO.	SrO.	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MgO.	CO <sub>2</sub> .	Ign.
38.74	trace	0.39	6.29	0.86	43.63	3.81

L. J. S.

**Refractive Indices of the Rhombohedral Carbonates.** P. GAUBERT (*Bull. soc. franç. min.*, 1919, **42**, 88—120).—The observed values of the refractive indices of isomorphous mixtures of these carbonates agree closely with those calculated from their chemical composition by the formulæ of Mallard. The following method for distinguishing magnesite from the other carbonates is given: The powdered sample is heated to a red heat and a drop of cobalt nitrate solution is added, after cooling. A bluish-green halo immediately develops around particles of all carbonates except magnesite. CHEMICAL ABSTRACTS.

**Wolframite (Ferberite and Hübnerite) from Japan.** KOTORA JIMBŌ (*Beitr. Min. Japan*, 1915, No. 5, 256—259).—Scheelite occurs with rock-crystal in quartz veins at Kurasawa,

Kai. It is sometimes replaced by brownish-black ferberite (anal. I), these pseudomorphs having been originally described as tetragonal iron tungstate under the name "reinite." Microscopic crystals of hair-brown to dark red hübnerite (anal. II) occur with scheelite in gold-quartz at Nishizawa.

	WO <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	Total.
I .....	75.214	24.372	0.185	—	—	99.771
II .....	74.25	3.18	20.84	1.01	trace	99.28

L. J. S.

**Thaumasite and Spurrite from California.** W. F. FOSHAG (*Amer. Min.*, 1920, 5, 80—81).—Small needles of thaumasite form interlaced masses and fibrous veins in a rock composed of äkermanite and spurrite (A., 1909, ii, 61) in the crystalline limestones at Crestmore, California (A., 1919, ii, 113). Analysis gave:

SiO <sub>2</sub> .	(Al,Fe) <sub>2</sub> O <sub>3</sub> .	CaO.	SO <sub>3</sub> .	H <sub>2</sub> O+CO <sub>2</sub> (ign.).	Total.
9.10	0.84	12.98	27.56	49.48	99.96

The spurrite shows polysynthetic twinning, and is optically negative with  $\alpha$  1.638,  $\beta$  1.676. Since the rock contains 4.64% CO<sub>2</sub>, it follows that spurrite forms half the mass. Thaumasite has evidently been derived from spurrite by the action of sulphated waters, although sulphates are rare in the deposit. L. J. S.

**Mineralogy of Korea (Chōsen).** NOBUYO FUKUCHI (*Beitr. Min. Japan*, 1915, No. 5, 207—227).—Sixty mineral species are described. Yellow to brown crystals of orthoclase with a violet-blue schiller (moonstone) from Sōzen gave K<sub>2</sub>O 6.43, Na<sub>2</sub>O 6.53%, D 2.60. Crystals of zircon from Jidō gave SiO<sub>2</sub> 33.06, ZrO<sub>2</sub> 63.32, Fe<sub>2</sub>O<sub>3</sub> 3.33, TiO<sub>2</sub> nil; total, 99.71. The material is colourless, but it shows a dark violet on the surface and along cracks. Several partial analyses are given of phlogopite, ranging from MgO 23.77, FeO 1.47% in the colourless variety to MgO 4.52, FeO 3.45% in the black. L. J. S.

**Crystalline Nodules in Agalmatolite from Mitsuishi, Japan.** HIDEYUKI AWAZU (*Beitr. Min. Japan*, 1915, No. 5, 298—299).—The minute crystals composing the nodules are colourless with a perfect cleavage, and are doubtfully referred to gibbsite. [The following analysis suggests, however, that the material consists of diaspore with intermixed opal, as described by Y. Chitani (*J. Geol. Soc. Tokyo*, 1915, 22, 384; see *Mineralogical Abstracts*, 1920, 1, 64).]

Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	CO <sub>2</sub> .	SiO <sub>2</sub> .	H <sub>2</sub> O.	Total.
70.43	0.32	0.01	0.03	0.35	14.37	14.38	99.89

L. J. S.

**Analcite from Maze, Japan.** SEIGO SHIMIZU (*Beitr. Min. Japan*, 1915, No. 5, 295).—The following analysis agrees with the formula Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, 4SiO<sub>2</sub>, 2H<sub>2</sub>O:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
54.68	23.05	nil	0.10	0.45	nil	13.50	8.70	100.38

L. J. S.

**Axinite Crystals from Japan.** MASAOKI HOSHINA (*Beitr. Min. Japan*, 1915, No. 5, 294—295).—Pale violet-grey axinite, forming with quartz the gangue of copper ores at Ōgiyama, gave:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	Ign.
45.20	15.61	6.84	6.33	22.80	0.82	0.32

L. J. S.

**Chlorite from Jōdoyama, Japan.** DENZŌ SATŌ (*Beitr. Min. Japan*, 1915, No. 5, 296—298).—Loose blocks occurring on the surface of the granite-gneiss mountain of Jōdoyama consist of an aggregate of garnet, quartz, calcite, and dark green chlorite. The last of these gave on analysis:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	Ign.	Total.	Sp. gr.
30.12	11.80	35.22	3.29	5.81	3.58	10.27	100.09	3.25

L. J. S.

**Epidote Crystals from Katakai, Japan.** KINZŌ NAKASHIMA (*Beitr. Min. Japan*, 1915, No. 5, 253—255).—Large, brownish-green to greyish-green crystals embedded in massive, milky quartz gave:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	H <sub>2</sub> O.	Total.
38.34	27.45	8.81	0.86	0.21	23.21	0.31	2.21	101.40

L. J. S.

**Diabantite, Stilpnomelane, and Chalcodite from Westfield, Massachusetts.** EARL V. SHANNON (*Proc. U.S. Nat. Mus.*, 1920, 57, 397—403).—The diabase exposed in the trap quarries of this district is more or less altered with the formation of dark green, earthy, chloritic decomposition products. These are usually not sufficiently pure for chemical investigation, but better material was obtained from certain fissures. I is the mean of four analyses of diabantite. This is dark green and clayey when wet, but on drying it shrinks and cracks to a friable, pale olive-green mass. D 2.77. The minute micaceous scales are optically negative and sensibly uniaxial. Heated in the closed tube, it becomes brown, yields neutral water, and finally fuses to a black, magnetic glass. It is readily soluble in hot hydrochloric or sulphuric acid, and less easily in nitric acid, in each case with the separation of flocculent silica. II is the mean of two analyses of stilpnomelane obtained from another fissure, but with the same general appearance as the diabantite; it is, however, more blue, more plastic, has a peculiar sub-metallic lustre, and the dried material is compact and tough. The two minerals can be distinguished by their behaviour in boiling nitric acid (D 1.20). Diabantite dissolves slowly without change, whilst stilpnomelane is wholly oxidised, yielding a rust-like, brown material. Analysis III is of chalcodite, which is found only in small amount as a scaly coating with a rich golden-yellow colour and metallic lustre. A minute amount

of pure material contained  $\text{SiO}_2$  45.77%, with much ferric iron, no ferrous iron, and very little alumina and magnesia. This is evidently an indefinite oxidation product of stilpnomelane; in some cases it still showed a green core containing ferrous iron.

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{FeO}$	$\text{MnO}$	$\text{CaO}$	$\text{MgO}$	$\text{H}_2\text{O}$ (at $105^\circ$ )	$\text{H}_2\text{O}$ ( $>105^\circ$ )	Total
I.	28.15	15.17	3.85	25.23	0.21	0.59	14.56	0.57	11.25	99.58
II.	44.08	4.74	5.27	23.31	0.87	trace	8.36	2.21	10.28	99.12
III.	44.64	6.75	23.59	—	—	—	—	6.21	7.14	98.19

L. J. S.

### The Cumberland Falls (Whitley Co., Kentucky) Meteorite.

GEORGE P. MERRILL, with analyses by EARL V. SHANNON (*Proc. U.S. Nat. Mus.*, 1920, **57**, 97—105).—This stone, which fell on April 9th, 1919 (this vol., ii, 47), represents a new type of meteorite, for which the name *Whitleyite* is suggested. It is a coarse breccia consisting of a chalky-white to grey portion in larger amount, with enclosed angular blocks of a black chondritic stone. The two portions each represent different types of stones, and the whole mass shows much evidence of crushing and distortion. The lighter-coloured portion (bulk analysis I) consists mainly of enstatite intimately intergrown with a monoclinic pyroxene, and with small quantities of diallage, nickel-iron, troilite, and graphite. The dark portion (bulk analysis II) owes its colour to finely-disseminated graphite and metallic particles:

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Cr}_2\text{O}_3$	$\text{P}_2\text{O}_5$	$\text{FeO}$	$\text{NiO}$
I.....	55.172	0.382	0.062	trace	2.916	0.123
II.....	41.683	1.537	0.591	trace	9.399	0.211
	$\text{CoO}$	$\text{CaO}$	$\text{MgO}$	$\text{MnO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$
I.....	trace	1.586	38.734	0.112	0.157	0.150
II.....	trace	4.059	27.848	—	trace	trace
	$\text{Fe}$	$\text{Ni}$	$\text{Co}$	$\text{Cu}$	$\text{Mn}$	$\text{Cr}$
I.....	0.888	0.059	0.004	0.003	0.005	trace
II.....	12.108	0.747	0.078	0.001	0.088	trace
	$\text{S}$	$\text{P}$	$\text{Cl}$	$\text{C}$	$\text{H}_2\text{O}$	Total (less O for Cl, S, P).
I.....	0.784	0.034	0.028	0.164	0.167	100.961
II.....	2.464	0.014	0.045	0.449	0.210	100.084

The percentage composition of the metallic portion of each is given under IA and IIA respectively:

	$\text{Fe}$	$\text{Ni}$	$\text{Co}$	$\text{Mn}$	$\text{Cu}$	$\text{Cr}$	Total
IA.....	92.596	6.152	0.417	0.522	0.313	trace	100.000
IIA.....	92.982	5.735	0.599	0.676	0.008	trace	100.000

IB is of the friable, chalky-white enstatite (with intergrown monoclinic pyroxene), forming the main mass of the lighter portion. IIB of the silicate (22.582%), decomposed by dilute hydro-

chloric acid; and IIc of the insoluble silicate (56·58%) in the darker portion:

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	NiO.	CoO.	MnO.	CaO.	MgO.	Ign.	Total.
I <sub>B</sub> ..	59·53	1·09	0·98	nil.	—	—	0·96	37·17	0·33	100·06
II <sub>B</sub> ..	38·239	trace	6·566	0·043	trace	0·709	5·246	49·197	—	100·000
II <sub>C</sub> ..	58·341	2·705	3·528	0·295	trace	0·562	5·073	29·496	—	100·000

From these analyses, the mineralogical composition of the dark enclosures is: metal, 13·022; troilite, 6·760; lawrencite, 0·080; chromite, 0·869; soluble silicates, mainly olivine, 22·582; insoluble silicates, mainly pyroxenes, 56·580; carbon, mainly amorphous, 0·449; calcium phosphate, trace; hygroscopic water, 0·210; total, 100·552.

L. J. S.

## Analytical Chemistry.

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**Filter with Perforated Plate and Wire Gauze.** F. MACH and P. LEDERLE (*Chem. Zeit.*, 1919, **43**, 831).—Silver gauze may be used in place of platinum in the filter described previously by the authors (A., 1919, ii, 303).  
W. P. S.

**Iron Basins and their Use in Analysis.** H. SERTZ (*Zeitsch. angew. Chem.*, 1920, **33**, i, 156).—Iron basins are useful for sulphide fusions, particularly when they have been treated previously with nitric acid.  
W. P. S.

**The Alteration of Glass Flasks used in Laboratories.** R. DUBRISAY (*Bull. Soc. chim.*, 1920, [iv], **27**, 409—411).—The physico-chemical volumetric method previously described (compare A., 1913, ii, 388) for the estimation of traces of alkali can be used for the estimation of the amount of alkali dissolved from glass vessels when water is boiled in them. The method has been applied to compare the resistance of some French flasks made during the war with that of some pre-war German flasks. The French flasks showed up very well, both in their resistance to attack by boiling water and by boiling alkali.  
W. G.

**Methyl-orange as Indicator.** V. MACRI (*Boll. Chim. farm.*, 1920, **59**, 193—196).—The author describes the behaviour of methyl-orange in presence of various compounds which affect its action as an indicator (compare *J. Soc. Chem. Ind.*, 1920, August).  
T. H. P.

**Use of Conductivity Titrations in Neutralisation Analysis.**  
**III. Titration of Combined Weak Acids or Bases in Salt (Displacement Curves).** I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, **111**, 97—108. Compare A., 1919, ii, 74, 76).—The quantity of a weak acid or base combined as a salt may



be estimated by titration with a strong base or acid, respectively, using the electrical conductivity as indicator. On adding a strong acid, say, hydrochloric acid, to the salt of a weak acid, the weak acid will be displaced, and, having a low degree of ionisation, the conductivity of the solution will change very little, but as soon as all the weak acid has been liberated, the first drop of strong acid in excess will cause a great increase in the conductivity. On plotting the conductivity against the number of c.c. of standard acid, a sharp break will be found, which represents the point of equivalence. The method is found to work well in all cases where, after displacement of 50% of the weak acid, the conductivity has not increased more than 1%. Examples are given of the titration of sodium acetate, sodium formate, and for weak bases, ammonium chloride. In the case of the dibasic acids in sodium oxalate, sodium tartrate, and sodium citrate, it is found that good results may be obtained here also, if in the last-named two cases an equal volume of alcohol is added to the solution before titration.

J. F. S.

**Spectrophotometric Study of the "Salt Effects" of Phosphates on the Colour of Phenolsulphonthalein Salts and some Biological Applications.** CHARLES L. BRIGHTMAN, M. R. MEACHEM, and S. F. ACREE (*J. Bact.*, 1920, **5**, 169—180. Compare A., 1919, ii, 75).—Phosphate solutions, varying in concentration from 0.5*N* downwards and showing the same hydrogen-ion concentration by the hydrogen electrode method, have a marked influence on the colour of phenolsulphonthalein salts. This salt effect becomes small when the phosphate concentration is 0.05*N* or less. The apparent ionisation constant of the phenolic group of the phenolsulphonthaleins varies with the concentration of the phosphate present, and averages about  $2.65 \times 10^{-8}$  when uncorrected for salt effect. When a graphic method is used for calculating the ionisation constant freed from the salt effect of phosphate, the value is lowered to about  $1.95 \times 10^{-8}$ .

CHEMICAL ABSTRACTS.

**Improved Form of McLeod Gauge.** AUSTIN BAILEY (*Chem. News*, 1920, **120**, 302).—A modification of the McLeod gauge, which consists mainly of a three-way tap which connects the mercury reservoir with either an aspirator or the air through a fine jet, and of a movable and interchangeable pressure chamber which permits of the gauge being used over large ranges of pressure. With this apparatus, the danger of the mercury rising too rapidly into the pressure chamber is avoided, because the air can only enter through the fine jet.

J. F. S.

**A Weight Burette for Gas Analysis.** E. R. WEAVER and P. G. LEDIG (*J. Amer. Chem. Soc.*, 1920, **42**, 1177—1185).—A weight burette is described for use in gas analysis. By means of

this, the volume of the sample and changes in volume after absorption of constituents are determined by weighing the quantity of mercury, after compensation, which is expelled from, or taken into, the burette. It is claimed that, with this device, the volumes obtained are very accurate, and the accuracy of the measurement is independent of the state of the meniscus. The readings are quite free from parallax errors, since no graduated scales have to be read. The gas to be measured never comes in contact with a stopcock, rubber tube, or other possible origin of a leak. The apparatus may be made of any desired size. A number of measurements are recorded, and it is shown that the average deviation from the mean value in a single gas estimation is 0.0044%, whilst the maximum divergence is only 0.014%.

J. F. S.

**Theory of the Katharometer.** H. A. DAYNES and G. A. SHAKESPEAR (*Proc. Roy. Soc.*, 1920, A, 97, 273—286).—The katharometer is an instrument designed for automatic registration of small quantities of hydrogen (1%—2%) in air; it is also of considerable use in determining the permeability of balloon fabric to hydrogen. In the present paper, an account is given of the instrument, and this is followed by a theoretical treatment of the principles involved in the use of the instrument. The instrument consists of two small helices of thin platinum wire (ca. 0.001 inch diam.) enclosed each in one of two cells in a copper block; each helix is mounted in a small frame consisting of a loop of copper wire soldered to a ring of copper. This ring is fitted with an insulating plug, through which the copper lead wire is introduced. One extremity of the helix is soldered to the lead and the other to the distal end of the loop. The outer part of the lead passes through a plug of rubber fitting into the cell, and over this rubber an ebonite plug is pressed down by a screw collar. Thus the cell is rendered gas-tight. Both cells are similarly fitted, except that, whilst one is hermetically sealed, the other communicates with the atmosphere by three small holes. The helices constitute two arms of a Wheatstone bridge, and have a resistance of about 8 ohms. The main working current of the bridge is 0.100 ampere, and this gives the wires a temperature about 15° above that of the copper block. Contact with hydrogen, owing to surface combustion, raises the temperature of one helix, and from the change in resistance the amount of hydrogen in the air may be estimated.

J. F. S.

**Titration of certain Chlorides with Silver Nitrate, using Potassium Chromate as Indicator.** H. W. BOLAM (*Chem. News*, 1920, 120, 292).—When barium, or other metal yielding a chromate less soluble than silver chromate, is present, slightly more chromate than is sufficient to precipitate the barium should be added before proceeding with the titration of a chloride with silver nitrate.

W. P. S.

**Gravimetric Analysis. XIII. Estimation of Sulphuric Acid. III.** L. W. WINKLER (*Zeitsch. angew. Chem.*, 1920, **33**, 159—160, 162—163. Compare this vol., ii, 329).—Tables are given showing the corrections to be applied to the weight of barium sulphate precipitates for the effect of alkali chlorides and other salts on the precipitation. The presence of ammonium chloride decreases the effect of other salts.

A summary is given of conditions of precipitation, and of corrections to be applied, as detailed in the earlier parts, in order to obtain trustworthy results. W. P. S.

**Estimation of Nitro-groups by a Modification of Young and Swain's Method.** LOUIS DESVERGNES (*Ann. Chim. anal.*, 1920, [ii], **2**, 141—143).—Many nitro-substances, when dissolved in sodium hydroxide solution, yield a brown coloration, which interferes with the iodometric estimation of the excess of stannous chloride used in Young and Swain's reduction method (*A.*, 1898, ii, 186); it is therefore recommended that alcohol be used for dissolving the substance. The alcoholic solution is heated for two hours with an excess of stannous chloride solution in an atmosphere of carbon dioxide, and the excess is titrated subsequently with iodine solution. The method is trustworthy with a large number of nitro-substances, but not so in the case of nitrophenols and nitronaphthalenes. W. P. S.

**Apparatus for the Estimation of Nitric Nitrogen by Devada's Method.** JOSEPH ERLICH (*Ann. Chim. anal.*, 1920, [ii], **2**, 143—153).—The apparatus consists of a flask in which the nitrate is reduced by means of Devada's alloy, a condenser, and a receiver. The flask is connected with the condenser by a bulbed tube containing glass balls to prevent spray passing over into the receiver; a tube extends down the centre of this bulbed tube, and is used for passing a current of air through the apparatus towards the end of the operation. W. P. S.

**Colour Changes of the Diphenylamine Reaction.** E. M. HARVEY (*J. Amer. Chem. Soc.*, 1920, **42**, 1245—1247).—A modified diphenylamine reagent for use in microchemical tests for nitrates consists of 0.05 gram of diphenylamine, 7.5 c.c. of sulphuric acid (95—96%), 2.5 c.c. of 10% aqueous potassium chloride solution; or, if it is particularly desirable to avoid darkening of tissue, 5 c.c. of sulphuric acid, 3 c.c. of glacial acetic acid, and 2 c.c. of 12% aqueous potassium chloride solution may be used, at some sacrifice of colour intensity. A diagram shows that over the ranges 0—41%, 41—46%, 46—83%, 83—87%, 87—100%, with maxima of intensity at 38%, 71%, and 100% of sulphuric acid, the colours observed are oriental green to yellow, bluish-green, blue, colourless, and purple, respectively. The proportion of diphenylamine is variable between fairly wide limits, but in excess it interferes with the reaction; variations of temperature between 20° and 50°

have little effect; potassium chloride causes not only an intensification of the blue colour, but an extension in both directions of the concentrations of sulphuric acid which produce it, and it is more suitable for this purpose than sodium chloride, owing to the greater solubility of its acid sulphate. The stability of the blue colour once produced, even in concentrations of acid in which normally it would not be produced, renders the order of mixing of some importance.

J. K.

**Denigès's Strychnine-Molybdate Reaction.** L. DÉBOURDEAUX (*Bull. sci. pharmacol.*, 1920, **27**, 70—72).—In order to detect phosphates in the presence of barium, the preparation of Denigès' strychnine-molybdate reagent has been modified as follows: Strychnine (1.17 grams) is dissolved on a boiling water-bath in 200 c.c. of water and 8 c.c. of nitric acid (1:9). Ammonium molybdate (75 grams) is dissolved in 50 c.c. of water, the solution is mixed while cold with 50 c.c. of nitric acid (D 1.20), digested at 40° for four days, and the clear solution decanted or filtered through glasswool. Thirty c.c. of this solution and 30 c.c. of nitric acid (1:9) are added to the strychnine nitrate solution, and the whole is made up to 300 c.c. The reagent thus prepared is at first colourless, but acquires finally the colour of picric acid, at which point it has reached its maximal sensitiveness. This occurs about the eighth or tenth day, although the reagent can be used on the third day. The sensitiveness persists for two to three months, but only 1% remains after five to six months. The sensitiveness depends largely on the molybdate solution, which must be freshly prepared as described.

CHEMICAL ABSTRACTS.

**Estimation of Small Amounts of Phosphoric Acid as Barium Phosphomolybdate in the Presence and in the Absence of Phosphorus in Organic Combination.** S. POSTERNAK (*Bull. Soc. chim.*, 1920, [iv], **27**, 507—518).—It is possible to estimate amounts of phosphorus as small as 0.05 mg. by precipitation and weighing as barium phosphomolybdate from the corresponding ammonium salt in a medium containing, in addition, only sulphate alone or nitrate alone.

In the absence of organic matter, the inorganic phosphorus is precipitated from hot solution in the presence of 5% of sulphuric acid and 10% of ammonium sulphate. The ammonium phosphomolybdate precipitate is washed four times with a 5% solution of ammonium nitrate, then dissolved in a little ammonia, and reprecipitated with a 10% solution of barium chloride. The precipitate is collected, washed with water, dried, and calcined at a red heat. It has the constitution  $4\text{Ba}_{27}[\text{PO}_4(\text{MoO}_4)_{12}]_2, \text{Ba}_9[\text{SO}_4(\text{MoO}_4)_8]$ , and its weight when multiplied by 0.00739 gives the weight of phosphorus present.

In the presence of organic compounds of phosphorus, the inorganic phosphorus is first precipitated at 15° in a medium containing at least 5% of ammonium nitrate. The precipitate of

barium phosphomolybdate finally obtained in this case has the constitution  $8\text{Ba}_{27}[\text{PO}_4(\text{MoO}_4)_{12}]_2\cdot\text{Ba}_4(\text{MoO}_4)_4$ , and the factor for converting its weight into weight of phosphorus is 0.00786. Under these conditions, none of the organic phosphorus is precipitated.

W. G.

**Presence of Phosphates in Human Blood. X. The Nephelometry of Phosphoric Acid in Analyses which deal with Quantities of the Order of Magnitude employed in Bang's Method as a Means of Studying the Distribution of Phosphorus, especially in Lecithinæmia.** JOH. FEIGL (*Biochem. Zeitsch.*, 1920, **102**, 131—141).—A detailed discussion of the technique of the above method.

S. S. Z.

**Some Quick Methods for [the Detection of] Arsenic and Antimony.** CHAS. W. CUNO (*Proc. S. Dakota Acad. Sci.*, 1919, **3**, 34—47).—The following methods are sensitive to 0.1%. (1) The substances in acid solution are precipitated by hydrogen sulphide, the precipitate is well washed and extracted several times with an ammoniacal solution of ammonium carbonate to remove arsenic sulphide, which is then reprecipitated by concentrated hydrochloric acid; copper interferes very little if the precipitate has been well washed. Antimony sulphide is removed from the precipitate by repeated washing with a hot solution of sodium carbonate; by using small quantities and re-heating each time, the antimony is obtained in concentrated solution, and separates, on cooling, almost quantitatively at 0°. Tin is removed from the sulphide precipitate by sodium hydroxide solution, and is detected in the usual way.

(2) When copper and mercury are not present, a solution of the ore in hydrochloric acid is treated with sodium thiosulphate, whereby arsenic, antimony, and bismuth are precipitated, but not cadmium and tin. The precipitate is boiled with concentrated hydrochloric acid, when the arsenic remains undissolved. When arsenic, antimony, tin, copper, cadmium, and bismuth are all present, the material is dissolved in hydrochloric acid, and the solution is warmed with a concentrated solution of sodium thiosulphate, whereby arsenic only is precipitated, together with some sulphur; by diluting the solution to six volumes and warming, antimony will first appear as a red coloration, which is quickly masked by the other metals.

(3) When copper is absent, arsenic can be detected by dissolving the substance in concentrated hydrochloric acid and passing a rapid stream of hydrogen sulphide into the concentrated solution; no other metal except copper is precipitated in concentrated hydrochloric acid solution.

CHEMICAL ABSTRACTS.

**Estimation of Small Quantities of Arsenic.** K. SCHERINGA (*Pharm. Weekblad*, 1920, **57**, 420—421).—A slight modification in the Bloemendal arsenic apparatus is described. The estimation

of arsenic in urine is carried out as follows: 500 c.c. of urine are evaporated to dryness with 30 grams of pure sodium chloride. The residue is transferred to a distillation flask, and 30 c.c. of pure concentrated sulphuric acid are added. As much as possible of the hydrogen chloride is distilled over and is absorbed in 100 c.c. of saturated sodium carbonate solution. To the solution, a slight excess of bromine is added, and then 5 c.c. of 10% sodium phosphate solution and 5 c.c. of ammoniacal magnesia mixture. The precipitate is dissolved in dilute sulphuric acid, reduced, and the solution transferred to the apparatus. This procedure is applicable to most organic substances containing arsenic. W. S. M.

**Rapid Estimation of Arsenic in Commercial Sulphuric Acid.** A. A. KOHR (*J. Ind. Eng. Chem.*, 1920, **12**, 580—581).—For the estimation of arsenious arsenic, 20 grams of acid are diluted with water, and a few drops of methyl-orange added. The solution is neutralised with sodium carbonate solution until it is very faintly pink, and about 2 grams of powdered sodium hydrogen carbonate are then added. The solution, after dilution with water to 250 c.c., is titrated with 0.1*N*-iodine and starch, a blank test being made. For determining the arsenic in the arsenic form, 20 grams of acid are heated for one hour in an oven at 105—110°. It is then diluted with a little water, and a saturated solution of sodium hydrogen carbonate added in slight excess, phenolphthalein being used as indicator. The solution is boiled and filtered. Three grams of powdered sodium hydrogen carbonate are added, and 150 c.c. of hydrochloric acid are slowly poured in with agitation, after which 1 gram of potassium iodide is added, and air excluded. After agitation and remaining for five minutes, the solution is titrated with 0.1*N*-thiosulphate and starch. The reaction,  $\text{H}_3\text{AsO}_3 + \text{I}_2 + \text{H}_2\text{O} = \text{H}_3\text{AsO}_4 + 2\text{HI}$ , proceeds from left to right when the concentration of the hydrogen ion is low; and there should be few OH ions. In presence of sufficient hydrogen chloride, the reaction goes from right to left. Copper salts interfere in the arsenic determination but are usually negligible. If in appreciable amount, they must be estimated, and a correction applied to the thiosulphate titration. W. J. W.

**The Acidimetric Estimation of Boric Acid.** J. A. M. VAN LIEMPT (*Zeitsch. anorg. Chem.*, 1920, **111**, 151—166).—See this vol., ii, 331.

**Estimation of Carbon Dioxide in Moorland Waters.** V. RODT (*Chem. Zeit.*, 1920, **44**, 469).—In titrating the free carbon dioxide and that present as hydrogen carbonates in moorland waters, errors are caused by the presence of weak organic acids and their salts, which are simultaneously titrated. Winkler's method (*Zeitsch. Nahr. Genussm.*, 1910, **20**, 617) of removing free carbon dioxide by repeatedly spraying the water would scarcely be applicable on a small scale. When the solvent action of moorland

water on limestone is to be determined, Heyer's method (*Gesundheitsing.*, 1912, **35**, 669) may be employed. The water is shaken at frequent intervals with powdered marble in a closed flask, and a portion then titrated with  $N/10$ -acid (methyl-orange as indicator). The difference between the result and that obtained by titrating the water, without treatment with marble, gives the amount of calcium carbonate dissolved by the water. C. A. M.

**Use of the Jamin Interferometer for the Estimation of Small Amounts of Helium or Hydrogen in Air.** J. C. McLENNAN and R. T. ELWORTHY (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 19—25).—A method for the estimation of small amounts of helium and hydrogen in air by means of the Jamin interferometer is described. Two methods of calibrating the instrument are outlined, one based on the relation between the difference in path caused by the displacement of air in one tube by the mixture and the resulting shift of bands, and the second based on the change of refractive index of the air in one tube caused by lowering the pressure of the air. The accuracy was  $\pm 0.5$  per cent. With longer tubes, a greater accuracy could be obtained.

J. R. P.

**Estimation of the Helium Content of Mixtures of Gases by the Use of a Katharometer.** V. F. MURRAY (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 27—35).—The Shakespear Hydrogen Purity Meter, high and low percentage explorers, and a Shakespear Permeameter Explorer have been calibrated for use with helium.

J. R. P.

**Application of a New Physico-chemical Method of Analysis to the Study of Double Salts.** RENÉ DUBRISAY (*Compt. rend.*, 1920, **170**, 1582—1584).—The method employed is based on the observation of the temperature of mixing the solutions with an invariable liquid (compare A., 1919, i, 73; ii, 78), phenol being used. If a mixture of solutions of sodium sulphate and potassium sulphate is thus mixed with phenol, the temperature of mixing observed agrees closely with that calculated from the law of additivity. If, however, a mixture of solutions of potassium sulphate and zinc sulphate is used, there is a variable difference between the observed and calculated results, the maximum variation corresponding with equimolecular proportions of the two salts, and indicating the presence, in solution, of a double salt. W. G.

**Estimation of Alkali as Sulphate with Special Reference to the Alkali Salts of Organic Acids.** C. F. VAN DUIN (*Chem. Weekblad*, 1920, **17**, 283—284).—The usual procedure is modified as follows: The alkali salt is evaporated with concentrated sulphuric acid until fuming ceases. The residue of sulphate and pyrosulphate is dissolved in ammonium carbonate solution. The solution is evaporated to dryness on asbestos and the residue gently ignited. In this way, no losses by spirting are incurred, and any carbonaceous matter is easily burned off. W. S. M.

**Sensitiveness and Applicability of Qualitative Reactions.**

**I. Potassium Ions.** O. LUTZ (*Zeitsch. anal. Chem.*, 1920, **59**, 145—165).—The sensitiveness of various reactions for potassium was determined, the different tests being made as far as possible under the same conditions. In each test, 5 c.c. of potassium chloride solution were treated with the reagent, the temperature was kept at 18°, and the observation made after five minutes' contact; the following are the minimum concentrations of potassium which gave a reaction with the reagents: perchloric acid, 1:435; phosphomolybdic acid, 1:561; platinum chloride, 1:587; sodium borofluoride, 1:970; aniline hydrosilicofluoride, 1:1022; sodium phosphotungstate, 1:2170; phosphotungstic acid, 1:2809; sodium cobaltinitrite, 1:25,000; sodium-bismuth thiosulphate, 1:57,000; sodium picrate, 1:840; sodium 1-amino- $\beta$ -naphthol-6-sulphonate, 1:1022; sodium hydrogen tartrate, 1:1050. It is suggested that the results might also be expressed in actual quantities of potassium; for instance, the concentration 1:435 (perchloric acid test) would be  $11 \times 10^{-3}$  grams of potassium per 5 c.c. W. P. S.

**Analysis of Ingredients for Pyrotechnics.** HENRY B. FABER and WILLIAM B. STODDARD (*J. Ind. Eng. Chem.*, 1920, **12**, 576—578).—Sodium nitrate occurring in potassium nitrate in quantities as low as 0.01% may be estimated by a modification of Ball's method (T., 1909, **95**, 2126; 1910, **96**, 1408).

Instead of a separating funnel, a series of 30 c.c. Erlenmeyer flasks may be used for the precipitation of the caesium sodium bismuth nitrite. One gram of potassium nitrate is dissolved in 5 c.c. of water, 1 c.c. of 2*N*-nitric acid added, and 10 c.c. of the reagent. The flasks are connected, and the air is displaced by coal gas, one end of the series then being closed by a plug and the other by a Bunsen valve. After remaining for forty-eight hours in a cool place, the precipitate is collected on a Gooch crucible and washed with dilute, and then pure, acetone, the process being carried out rapidly to minimise exposure to air. The crucible is finally dried in an air-bath at 100° for thirty minutes, and the weight of sodium calculated from the weight of precipitate  $\times 0.03676$ . Alternatively, the precipitate may be treated with 150 c.c. of water, 0.1*N*-potassium permanganate added in excess, and 40 c.c. of sulphuric acid (1:1), the solution being heated to 70° and titrated with 0.1*N*-sodium oxalate. The available oxygen of the permanganate consumed  $\times 7.820$  gives the weight of caesium sodium bismuth nitrite.

For the determination of nitrates, 1 gram is mixed with 5 grams of tungsten trioxide in a platinum crucible and heated over a Bunsen for ten minutes. The loss in weight represents oxygen and oxides of nitrogen, and enables the percentage of pure nitrate to be calculated.

For estimating aluminium in flakes or powders, its reducing power on lead oxide is utilised. Three grams of aluminium are mixed with 100 grams of litharge and 30 grams of borax glass in



a fireclay crucible, a covering layer of 25 grams of borax glass being added. The mass is fused in a muffle for twenty minutes. The lead is then separated from the slag and weighed, the factor 0.0872 giving the equivalent aluminium. A high temperature should be employed to reduce the time of fusion and minimise re-oxidation of the lead.

W. J. W.

**A Method for the Determination of the Ion Concentration in Ultra Filtrates and other Protein-free Solutions.**

BRINKMAN and (Miss) E. VAN DAM (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 762—771).—A simple method for measuring the concentration of calcium ions in a solution of a mixture of salts is based on the following principle. To a solution containing  $\text{Ca}^{++}$ , there are added oxalate ions until the solubility of calcium oxalate is just reached. A slight milkiessness appears directly this point is passed. The method is correct to 2—3 mg. of calcium per litre. The principle of the method can be applied to the estimation of other ions. The only condition is the employment of a reagent that will give a very sparingly soluble salt with the ion the concentration of which is to be measured.

J. C. D.

**Colorimetric Method for the Estimation of the Copper and Iron Present in Lead and Lead Oxides.**

CHARLES R. HARDY (*Chem. News*, 1920, **120**, 256).—A rapid method of estimating small quantities of iron and copper in metallic lead or litharge. The sample (200 grams) is dissolved in nitric acid (D 1.2) and diluted as the action proceeds to prevent lead nitrate crystallising. The solution is treated with concentrated sulphuric acid (32 c.c. per 100 grams of sample) and the precipitate allowed to settle. The solution is decanted four or five times, treated with 10 c.c. of sulphuric acid, and evaporated nearly to dryness. After cooling, the liquid is diluted with water and filtered. The filtrate is evaporated to small bulk, treated with a few drops of nitric acid, boiled and treated with ammonia. The precipitate is filtered, redissolved, and reprecipitated. The filtrates from the iron contain all the copper; these are evaporated and the volume made up to 50 c.c. The measured quantity is made ammoniacal and boiled until quite neutral. When cold, the solution is placed in a Nessler glass, 5 c.c. of potassium ferrocyanide solution (0.4%), and 5 c.c. of ammonium nitrate solution (10%) added. In a second Nessler glass, 5 c.c. of ferrocyanide and 5 c.c. of ammonium nitrate are placed, and the volume made the same as that in the first glass with distilled water. A standard solution of copper (0.393 gram  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  per litre) is added from a burette until the colour in both glasses is the same.

The iron precipitate is dissolved in a small quantity of nitric acid and made up to 250 c.c.; 25 c.c. is placed in a Nessler glass with 9 c.c. of 25% hydrochloric acid and 5 c.c. of ammonium thiocyanate solution (5%). In a second glass, 10 c.c. of 25% hydrochloric acid and 5 c.c. of thiocyanate solution are placed, and the volume made up to that in the first glass. A standard iron solu-

tion (0.210 grams ferrous ammonium sulphate per litre) is then run in from a burette until the tints of both are alike.

If red lead has to be examined, a 20-gram sample should be taken, dissolved in aqua regia, and sufficient water added to dissolve all the lead chloride. J. F. S.

**Assay of Alunite.** EDWARD S. SIMPSON (*Chem. Eng. Min. Rev. Australia*, 1919, **11**, 297—298).—The estimation of the total alunite is based on the fact that alunite is the only sulphate in the ore which is insoluble in water, but soluble in dilute sodium hydroxide solution; not uncommonly, a little calcium and magnesium sulphates are present, for which a correction must be made. Sulphates soluble in water are estimated by treating 0.7 to 0.8 gram of the ore with 100 c.c. of water, and after one hour estimating the dissolved sulphates as barium sulphate. Total sulphates are estimated by heating 0.7 to 0.8 gram of the ore with 60 c.c. of 5% sodium hydroxide solution on the steam-bath for one hour, with occasional stirring, and estimating the sulphate in the filtrate as barium sulphate. From the total sulphate are subtracted the sulphate found in a blank experiment and the water-soluble sulphate; the difference, expressed as a percentage of the ore and multiplied by 2.55, gives the percentage of alunite (including natro-alunite). The error may be +2%.

The estimation of the extractable alkali oxides in the ore is performed by heating 0.5 to 0.6 gram of the ore in a muffle furnace at 819° during one hour (freshly fused sodium chloride is used to indicate the temperature; the temperature must not exceed 877° [m. p. of lead oxide]), and, after cooling and weighing, extracting the residue with boiling water and treating the filtrate with 7 c.c. of barium chloride solution (122 grams in a litre) and 0.6 gram of hydrated barium hydroxide; after removing the excess of barium and the calcium in the usual way, the total alkali chlorides and the potassium chloride (as platinichloride) are estimated by the usual methods. The results, corrected by the amounts found in a blank experiment, are expressed as percentages of the raw ore and of the roasted ore. CHEMICAL ABSTRACTS.

**Rapid Volumetric Method for the Estimation of Iron, Applicable in the Presence of Hydrochloric Acid, Phosphorus, Oxy-acids, and Organic Matter.** H. DROOP RICHMOND and EDITH M. ISON (*Analyst*, 1920, **45**, 258—260).—The following method gives trustworthy results for the estimation of iron in many pharmaceutical preparations. From 5 to 10 c.c. of the sample are treated with a few drops of hydrochloric acid, and *N*/10-permanganate solution is added until a transitory purple coloration is produced throughout the solution. An equal volume of concentrated hydrochloric acid is then added, followed by a small quantity of sodium hydrogen carbonate (to give an atmosphere of carbon dioxide), and *N*/10-stannous chloride solution is run in drop by drop until a drop of the mixture gives a blue

coloration with potassium ferricyanide solution. The mixture is then titrated with *N*/10-stannous chloride solution, using thiocyanate solution as an external indicator. The number of c.c. of *N*/10-stannous chloride solution used in the titration is multiplied by 0.0056 to obtain the quantity of iron present. W. P. S.

**Estimation of Iron and Separation of Manganese from Iron by the Ammonium Salt of Nitrosophenylhydroxylamine (Cupferron).** E. H. ARCHIBALD and RUTH V. FULTON (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 243—253).—The cupferron precipitate of iron is slightly soluble in the acid solution from which it is precipitated. The solubility is apparently not affected by the substitution of sulphuric for hydrochloric acid, but is appreciably lowered by adding ammonium chloride to the solution. The precipitate is slightly soluble in the wash-water. If corrections are applied for these solubilities, the method is very exact. Iron can be separated from manganese in a solution containing four times as much manganese as iron, the amount of manganese carried down by the precipitate being inappreciable for most purposes. The amount increases with the acid dilution of the mother liquor. The presence of ammonium chloride to the extent of 5 grams in 100 c.c. of solution is an advantage in the separation. J. R. P.

**Use of the Rotating Zinc Reductor in the Estimation of Molybdenum.** WALTER SCOTT (*J. Ind. Eng. Chem.*, 1920, **12**, 578—580).—The rate of reduction of molybdic acid by zinc is nearly as rapid between 20° and 30° as at the boiling point. Reduction is not appreciably affected by the aid of an electric current. By covering the beaker with a split cover-glass during the operation, enough hydrogen is retained to act as a protective covering for the zinc. The reduced solution may be titrated with permanganate in the same beaker; if it is transferred to another vessel, it must be poured into ferric alum and syrupy phosphoric acid. W. J. W.

**Bibliography of the Analysis of Antimony.** ELTON R. DARLING (*Chem. Eng.*, 1919, **27**, 11—12, 63; from *Chem. Zentr.*, 1919, ii, 890; 1920, ii, 750).—A compilation of English, French, and German literature on the subject. E. H. R.

**Process for Testing Air for the Presence of Combustible Substances.** E. BECKMANN [with KURT STEGLICH] (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1914, **34**, 924—936).—Two pieces of apparatus have been designed, primarily to test the air of coal mines in respect of explosibility due to the presence of methane. That for the preliminary test consists of a cylinder fitted with a piston and inlet valve for collection of the sample, which is exploded by means of pyrophoric iron, the heat generated causing a temporary expansion, which is registered by a manometer. A locking device ensures that the igniter shall not be operated until

the inlet valve is closed. Explosion only takes place when 7—10·3% of methane is present, but the limits can be widened somewhat by compression of the gas and by use of a catalyst, although its untrustworthiness renders the latter not very suitable for practical purposes. Addition of methane or air with the same object to samples outside the limits given is also liable in practice to lead to erroneous results. The second apparatus is a metal cylinder, containing potassium hydroxide, connected to a suction pump which serves to fill the vessel with air to be tested, and to a mercury manometer which indicates the contraction due to absorption of the carbon dioxide and water resulting from combustion of the methane. Ignition is secured by a platinum spiral, made white-hot by a current for the space of two minutes, the time being regulated by a mercury contact on the principle of the ordinary sand-glass. A non-return valve protects the manometer from the initial force of explosion, and provision is made for the automatic sounding of an electric alarm to follow a contraction due to a proportion of methane in excess of the safety limit. A determination takes about three minutes, and a form of the apparatus has been developed by which analyses are automatically made and registered every half-hour. As the gas examined is not filtered, any dust present exerts the same effect as it would do in an actual explosion. The explosions diminish in intensity with increase in the proportion of methane, and no longer occur when this reaches 16%. Further, in consequence of the increasing formation of carbon monoxide and hydrogen in these circumstances, the degree of contraction observed gradually diminishes and gives place to an expansion when 20% or more of methane is present. Any uncertainty as to the meaning of a small contraction is removed by repetition of the determination after admixture of air with the gas under examination. Hydrogen and illuminating gas may be detected by the first apparatus between limits of 9 and 42%, 8 and 25% respectively; further, the fact that a red heat suffices to initiate their combustion in the second apparatus supplies a means of detecting these gases in presence of methane. J. K.

**Estimation of Acetylene in Coal Gas and Air by Means of Ilosvay's Reagent.** H. ARNOLD, E. MÖLLNEY, and F. ZIMMERMANN (*Ber.*, 1920, **53**, [B], 1034—1039. Compare Ilosvay de Nagy Ilosva, A., 1900, ii, 52).—The coal gas is shaken in a separating funnel of about 3 litres capacity with about 20 c.c. of the reagent at intervals during an hour; the precipitate is filtered and well washed with water containing hydroxylamine. The precipitate and filter are treated in a crucible with a little concentrated nitric acid, the solution is evaporated, and the residue ignited and weighed as copper oxide. The results obtained in this manner are sometimes high, due to the presence of impurities derived from the reagents in the precipitated copper acetylide, but this drawback may be overcome by dissolving the precipitate from the filter with nitric acid and evaporation of the filtrate.

Test analyses with mixtures of acetylene and air show the method

to be very accurate, and to be available even when not more than 0.04% of acetylene is present; at such dilutions, however, it is necessary to add about 5% of carbon dioxide to the mixture, since otherwise the results are low as a consequence of atmospheric oxidation. The process can also be used for the estimation of acetylene in coal gas, from which hydrogen sulphide, if present, must be removed; this can be effected by dry copper sulphate-pumice.

H. W.

**Volumetric Estimation of Acetylene.** RICHARD WILLSTÄTTER and ERNST MASCHMANN (*Ber.*, 1920, **53**, [B], 939—941).—Methods of estimating acetylene, which are based on its reaction with silver nitrate and titration of the nitric acid liberated in accordance with the equation  $C_2H_2 + 3AgNO_3 = C_2Ag_2, AgNO_3 + 2HNO_3$ , are found to be untrustworthy, since it has not been found possible to find conditions under which a molecule of the gas liberates two molecules of nitric acid, the amounts of acid actually set free varying from about 0.5 mol. in alcoholic, to about 1 mol. in aqueous solution. The following procedure gives trustworthy results. Acetylene, in gaseous form or in solution, is agitated for a few minutes with Ilosvay's reagent freshly prepared from copper nitrate, ammonia, and hydroxylamine hydrochloride, and the precipitated copper acetylide is filtered through an asbestos filter and washed until the filtrate no longer decolourises *N*/10-permanganate, care being taken not to allow the precipitate to become dry. The copper acetylide is washed from the asbestos by means of about 25 c.c. of a solution prepared by making up ferric sulphate (100 grams) and concentrated sulphuric acid (200 grams) to a litre with water. The ferrous sulphate, formed in accordance with the equation  $C_2Cu_2 + Fe_2(SO_4)_3 + H_2SO_4 = FeSO_4 + 2CuSO_4 + C_2H_2$ , is estimated by titration with *N*/10-permanganate. The liberated acetylene does not introduce any complication. Test analyses with pure and diluted acetylene show the method to be accurate.

H. W.

**Estimation of Chloroform and other Volatile Substances.**

A. SCHLICHT and WALTER AUSTEN (*Zeitsch. öffentl. Chem.*, 1920, **26**, 55—57).—To estimate chloroform in admixture with alcohol, 5 c.c. of the mixture are diluted with water to 200 c.c. and shaken with 60 c.c. of ether; after the ethereal layer has separated, its specific gravity is determined. An increase of 0.0001 in the specific gravity corresponds with 0.1786 gram of chloroform in 100 c.c. of the original mixture.

W. P. S.

**Thermal Analysis of the Products of Nitration of Naphthalene.** P. PASCAL (*Bull. Soc. chim.*, 1920, [iv], **27**, 388—408).—A study of the melting-point curves of the binary mixtures, naphthalene- $\alpha$ -nitronaphthalene; 1:5-dinitronaphthalene-1:8-dinitronaphthalene;  $\alpha$ -nitronaphthalene-1:5-dinitronaphthalene;  $\alpha$ -nitronaphthalene-1:8-dinitronaphthalene; 1:5-dinitro-

naphthalene-1:3:5-trinitronaphthalene; 1:8-dinitronaphthalene-1:3:5-trinitronaphthalene; 1:5-dinitronaphthalene-1:3:8-trinitronaphthalene; 1:8-dinitronaphthalene-1:3:8-trinitronaphthalene; 1:3:8- and 1:2:5-trinitronaphthalenes; 1:3:5- and 1:2:5-trinitronaphthalenes; 1:3:5- and 1:3:8-trinitronaphthalenes; 1:4:5- and 1:3:8-trinitronaphthalenes; 1:4:5- and 1:2:5-trinitronaphthalenes; and of the ternary mixtures, nitronaphthalene and the two dinitronaphthalenes; the two dinitronaphthalenes and each of the trinitronaphthalenes in turn; 1:3:5-, 1:3:8-, and 1:2:5-trinitronaphthalenes. The application of these results to the analysis of industrial products of nitration of naphthalene is discussed.

W. G.

**Estimation of Methyl Alcohol.** A. HEIDUSCHKA and L. WOLF (*Pharm. Zentr.-h.*, 1920, **61**, 361—366).—The methyl alcohol is heated at 100° for an hour in a closed vessel with sulphuric acid and an excess of potassium dichromate; the quantity of carbon dioxide formed is then estimated gravimetrically by absorption in potassium hydroxide solution. The excess of dichromate is estimated volumetrically, and the quantity of methyl alcohol present is calculated from the weight of carbon dioxide formed or from the amount of oxygen required for the oxidation. The method may be applied to a mixture of methyl and ethyl alcohols, an allowance being made for the fact that 0.8% of the ethyl alcohol is also oxidised to carbon dioxide. [See, further, *J. Soc. Chem. Ind.*, 1920, 558A.]

W. P. S.

**Estimation of Ethylene Glycol.** BERNHARD MÜLLER (*Chem. Zeit.*, 1920, **44**, 513—515).—Ethylene glycol, now used as substitute for glycerol in Germany, may be estimated by the dichromate or acetin methods used in glycerol analysis, but the acetin method cannot be used for dilute solutions of the glycol. Oxidation with chromic acid and sulphuric acid, and gravimetric estimation of the carbon dioxide produced, also yields trustworthy results. Ethylene glycol does not appear to be oxidised completely to oxalic acid by permanganate in alkaline solution.

W. P. S.

**Analysis of Powders and Explosives. Differentiation of Glyceryl Trinitrate and of Ethylene Dinitrate.** M. D. MARQUEYROL and E. GOUTAL (*Bull. Soc. chim.*, 1920, [iv], **27**, 443—448).—When exposed in a desiccator over sulphuric acid at 12° and at the ordinary pressure, glyceryl trinitrate does not lose in weight, whereas ethylene dinitrate loses steadily. When a mixture of the two is so exposed, the loss in weight is directly proportional to the percentage of the latter in the mixture.

In 10% solution, glyceryl trinitrate and ethylene dinitrate cause respectively a lowering of 2.13° and 3.06° in the freezing point of benzene. With mixtures, the lowering is proportional to the amounts of the two substances present.

Either of these methods may be used for estimating the amount

of ethylene dinitrate in a sample of glyceryl trinitrate, and neither is vitiated by the presence of commonly occurring impurities, such as vaselin, diphenylamine, etc.

W. G.

**Estimation of Glyceryl Nitrate.** H. DROOP RICHMOND (*Analyst*, 1920, **45**, 260—265).—A method for the analysis of commercial "nitroglycerin" solution consists in diluting 10 c.c. of the sample with 50 c.c. of water and titrating the acidity with *N*/10-barium hydroxide solution; 0.1 c.c. is deducted from the volume of the latter solution required, and the result is divided by 1.02. To estimate the glyceryl nitrate, 5 c.c. of a 10% solution plus 5 c.c. of 90% alcohol, or 10 c.c. of a 5% solution, are treated with 25 c.c. of *N*/2-alcoholic sodium hydroxide solution; 20 c.c. of a 1% solution require 10 c.c. of the alkali solution. After five minutes, phenolphthalein is added, and the excess of alkali titrated with *N*/1-acid. If more than 4 c.c. of acid is used, the estimation must be repeated, increasing the quantity of alcohol, as the amount of water introduced must not exceed 10% of the total volume. The volume of alkali solution absorbed is corrected for the acidity; each c.c. of *N*/1-sodium hydroxide solution corresponds with 0.05675 gram of nitroglycerol. If 2 c.c. of 100 vol. hydrogen peroxide are added before the alkali is introduced, the final alcoholic strength has much less influence on the titration.

W. P. S.

**Volumetric Estimation of  $\beta\beta$ -Dichloroethyl Sulphide.** WILLIAM FRANCIS HOLLELY (T., 1920, **117**, 898—902).

**The Analysis and Composition of "Cresylic Acid."** J. J. FOX and M. F. BARKER (*J. Soc. Chem. Ind.*, 1920, **39**, 169—172T).—The "cresylic acid" used consisted of the tar acids distilling up to 210° and then refractionated up to 203° or 204°, such a fraction usually containing less than 10% of phenol. If more phenol is present, its proportion should be brought below 10% by adding a suitable amount of *m*-cresol. It is shown that Raschig's nitration process (A., 1900, ii, 694) for the estimation of *m*-cresol is sufficiently accurate for technical purposes. The authors obtained the best results by a slightly modified procedure in the first stage of the process. Ten grams of the "cresylic acid" are heated with 15 c.c. of 98% sulphuric acid in a 1200 c.c. flask until the liquid is viscous at the room temperature. By rotation, the liquid is spread in a thin layer over the bottom of the flask and 100 c.c. of nitric acid (D 1.4) is added, and the flask replaced on the water-bath. Raschig's procedure is then followed.

The following bromination method will give accurate results. One gram of the dried "cresylic acid" is weighed into a tared flask fitted with a ground-in stopper carrying a tap-funnel and an exit tube with a stopcock. Excess of a 20% solution of bromine in carbon tetrachloride is added drop by drop, and the mixture left for several hours. It is then warmed at a temperature not

exceeding  $50^{\circ}$  to expel bromine, and finally the solvent is distilled off under reduced pressure. The products of bromination are then weighed. The percentage of *m*-cresol is given by the equation  $\%m\text{-cresol} = (100W - 246.3)/0.731$ , where  $W$  is the weight of bromo-derivative obtained from 1 gram of the mixed cresols.

A modification of the method of Ditz and Cedivoda (A., 1900, ii, 54), in which the amount of bromine absorbed during bromination is estimated volumetrically, was found to be very rapid and sufficiently accurate for general work.

By estimating the percentage of *m*-cresol by one of these methods, and the percentage of phenol by the method previously described (A., 1917, ii, 513), or that of Dawson and Mountford (T., 1918, 113, 923), and determining the  $D_{555}^{15.5}$  of the mixture of cresols, the percentage of *o*-cresol present is given by  $0.0128O = 100(G - 1.0388) - 0.0386P$ , where  $O$  is the percentage of *o*-cresol,  $P$  that of phenol, and  $G$  the value of  $D_{555}^{15.5}$ . The percentage of *p*-cresol is then obtained by difference from 100.

Finally, the authors reply to the criticisms of Dawson and Mountford (*loc. cit*) of the curves given in their last paper (compare A., 1918, i, 427).

W. G.

**Titration of Sugars.** N. SCHOORL (*Zeitsch. Nahr. Genussm.*, 1920, 39, 180—182).—In the method described by Rupp and Lehmann (A., 1909, ii, 442) and Schowalter (A., 1919, ii, 172), the prescribed quantities of solutions must be employed in order that the tables may indicate the correct amount of dextrose. When an aliquot portion of the copper solution is titrated, the result must be corrected to the total volume before reference is made to the tables.

W. P. S.

**Detection of Oxalic Acid and Lactic Acid and Differentiation from Tartaric Acid.** KURT BRAUER (*Chem. Zeit.*, 1920, 44, 494).—When heated with a mixture of concentrated sulphuric acid and resorcinol, oxalic acid yields a brilliant violet coloration, whilst tartaric acid and lactic acid give red colorations. Tartaric acid gives a yellow, oxalic acid a green, and lactic acid a red coloration when heated with dilute sulphuric acid (1:1) and resorcinol. The colorations obtained are less characteristic when the resorcinol is replaced by phloroglucinol, catechol, or quinol.

W. P. S.

**A Reaction of Benzoic Acid Based on its Diazotisation; Its Application to the Toxicological Detection of Atropine, Cocaine, and Stovaine.** MARCEL GUERBET (*Compt. rend.*, 1920, 171, 40—41).—The following procedure gives a ready means of detecting as little as 0.0001 gram of benzoic acid, or of substances such as cocaine or stovaine which contain a benzoyl group, or of atropine which on oxidation yields benzoic acid. The small amount of material is placed on a watch-glass, three or four drops of nitric acid ( $D\ 1.49$ ) are added, and the mixture evaporated to dryness



on a water-bath. The residue is taken up with one drop of a 10% solution of stannous chloride, and after two or three minutes' warming, the nitrobenzoic acids are reduced. The liquid is allowed to cool, and two drops of a 1% solution of sodium nitrite are added, and finally, three drops of a 1% solution of  $\beta$ -naphthol in ammonia, when a bright orange-red precipitate is obtained if benzoic acid or one of the alkaloids mentioned above was originally present. The test may be confirmed by dissolving the azo-compound in 1 c.c. of concentrated sulphuric acid and pouring the solution into water, an orange-yellow colour resulting.

For toxicological work, the test may be applied to the extracts of organs prepared by Stas's method. W. G.

**Analysis of "Saccharin."** OSKAR BEYER (*Chem. Zeit.*, 1920, **44**, 437—438).—To estimate *o*-benzoic sulphinide in commercial "saccharin," 1 gram of the sample is titrated with *N*/10-potassium hydroxide solution, using phenolphthalein as indicator; the percentage quantity ( $x$ ) is then calculated from the formula

$$x = 2.01329 \times c - 100/0.09845,$$

where  $c$  is the number of c.c. of *N*/10-solution used. The difference between the result and 100 gives the amount of *p*-sulphamino-benzoic acid present, provided other impurities are absent.

W. P. S.

**Estimation of Acetaldehyde in Paracetaldehyde.** F. von BRUCHHAUSEN (*Apoth. Zeit.*, 1919, **34**, 428—429).—A description of experiments in view to the adaptation of an iodometric method, similar to that employed by Romijn in the case of formaldehyde, for estimating acetaldehyde in paracetaldehyde, whereby only negative results were obtained. Richter's sulphite method is best suited to the problem in question. CHEMICAL ABSTRACTS.

**Estimation of Phytin in Plant Extracts.** AUGUST RIPPEL (*Biochem. Zeitsch.*, 1920, **103**, 163—172).—Phytin can be precipitated more or less quantitatively in the presence of inorganic phosphates by copper acetate in acetic acid solution. Favourable results can only be obtained with definite concentrations of copper acetate and acetic acid. An extract from barley yielded 63.3% of the phytin- $P_2O_5$  by precipitation with copper acetate in a 1% acetic acid. The same method accounted for 92.8% of the phytin in standard solutions of that substance. The phytin in an acetic acid extract from peas could not be precipitated by copper acetate at all. S. S. Z.

**A New Microchemical Reaction of Cystine Applicable to its Detection in Urinary Calculi.** G. DENIGES (*J. soc. pharm. Bordeaux*, 1920, **58**, 8—12).—After pointing out the disadvantages of the methods in use at present, the author describes the following modified Esbach method for the identification of cystine in urinary calculi. A small quantity (1 mg. or more) of

the powdered or finely shaved material is placed on a glass slide, moistened with a drop of concentrated hydrochloric acid (D at least 1.17 or 1.18) added at the outer edge by means of a pointed glass rod, and examined under the microscope without the use of a cover-glass. The groups of prismatic needles, which rapidly increase in number, are cystine hydrochloride, and can be distinguished even with low magnification. After a few minutes, a drop of water is stirred in. The crystals will be observed to dissolve. This is characteristic of cystine hydrochloride, and serves to distinguish it from uric acid, which is insoluble under these conditions. The solution is evaporated to dryness over a flame, the residue is cooled, covered with a slip, and a drop of water is added at the edge. The formation of hexagonal plates of cystine will be observed after a few seconds. Two photomicrographs are presented showing the crystalline forms described.

## CHEMICAL ABSTRACTS.

**Estimation of Urea by Means of the Carbon Dioxide Evolved by Urease.** S. PARTOS (*Biochem. Zeitsch.*, 1920, 103, 292—299).—An apparatus is described by means of which urea is estimated from the carbon dioxide evolved from it by urease. Estimations of urea in artificial preparations, as well as in urine, are described which show only an error of the order of about 1%.

S. S. Z.

**Rapid Detection of Morphine in the Toxicological Analysis of Viscera.** LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1918, 6, 349—351).—By means of the following method morphine was detected in the viscera after ingestion by the subject of only 0.002 gram: 120 grams of viscera are mixed with magnesia to a compact paste, which is completely dehydrated on the water-bath. The powdered residue is boiled with acetone, and the filtered extract treated with 2—3 c.c. of water and a few drops of acetic acid. The liquid is again filtered and evaporated on the water-bath. The residue containing the morphine is purified by treatment with 5% acetic acid, filtration, and extraction with boiling chloroform after addition of excess of ammonia.

W. R. S.

**Reduction Potentials of Mixtures of Indigotin and Indigo-white, and of Mixtures of Methylene-blue and Methylene-white.** W. MANSFIELD CLARK (*J. Washington Acad. Sci.*, 1920, 10, 255—270).—Measurements were made at 30° of the reduction potential of indigotinsulphonic acid and of methylene-blue solutions during titration with titanium trichloride over a considerable range of  $P_H$  values, from 1.55 to 8.58. To obtain the required values of the hydrogen-ion concentration, "buffer" salts were used, consisting either of citrate or mixtures of this with other salts. It was found that the sharpness of the end-point depended on the  $P_H$  value of the solution. This accounts, perhaps, for the empirical observation of Knecht and Hibbert, that a sharp end-point in the titration of many dyes with titanium trichloride

can only be obtained in presence of such substances as tartrates. In the case of indigotinsulphonic acid, the reduction potential varied from  $+0.2076$  at  $P_H=1.55$  to  $-0.1609$  at  $P_H=8.58$ , and with methylene-blue from  $+0.3811$  to  $-0.05$  over the same range.

E. H. R.

**Goiffon's Colorimetric Method for the Estimation of Stercobilin.** V. BORRIEN (*Compt. rend. Soc. Biol.*, 1920, **83**, 211—212; from *Chem. Zentr.*, 1920, ii, 723).—In Goiffon's method (this vol., ii, 399) a portion of the hydrobilirubin is carried down by the precipitate and remains on the filter. The accurate estimation of the substance is only possible when it has been isolated in the chemically pure condition, which has not been effected up to the present. For clinical purposes, methods such as that of Triboulet, which permit a rapid approximate estimation of the dye, are sufficiently accurate.

H. W.

**Estimation of Albumin in Urine containing Pus.** LUIS ESPINOSA TAMAYO (*Bol. Lab. Mun. Guayaquil*, 1920, **1**, 33).—One hundred c.c. of filtered urine are treated with 1 c.c. of strong ammonia, stirred, and left to settle for a short time; in the presence of pus a gelatinous precipitate is formed, which is filtered off. The filtrate is treated with 20 c.c. of sodium chloride solution and 30% trichloroacetic acid to acid reaction; after half an hour's heating on the water-bath the precipitate is collected on a tared filter, and the determination completed as in Scherer's method. The albumin is easily filtered off.

W. R. S.

**Van Deen's Reaction and Hydrocyanic Acid.** LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1918, **6**, 508—512).—Experimental proof is given that hydrocyanic acid, contrary to Selmi's statement (*Accad. Sci. Bologna*, 1879), does not interfere with Van Deen's reaction; on the other hand, potassium cyanide prevents the production of the blue coloration given by the reagent (hydrogen peroxide and tincture of guaiacum resin) in presence of fresh blood. This is shown to be due to the alkalinity of ordinary cyanide, as a positive reaction is obtained after neutralisation of the free alkali with acetic acid. Selmi's negative results must be attributed to the alkalinity of the cyanide used.

W. R. S.

**The Carbon Dioxide Content as a Basis for Distinguishing Heated from Unheated Milk.** LUCIUS L. VAN SLYKE and RICHARD F. KEELER (*J. Biol. Chem.*, 1920, **42**, 41—45).—It appears that normal unheated milk seldom, if ever, has a vol. % of carbon dioxide lower than 3.5—3. Pasteurisation reduces this value to 2.5 or less. Therefore, it appears safe, in general, to assume that milk containing less than 2.5 or 3 vol. % of carbon dioxide has been heated to the temperature of pasteurisation.

J. C. D.

## General and Physical Chemistry.

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**Arc and Spark Spectra and the Periodic System.** INGO W. D. HACKH (*Astrophys. J.*, 1918, **48**, 241—255).—A survey of the relations among number and intensity of lines in the arc and spark spectra and the *E.M.F.* and valency of elements. It is shown that elements of high electro-potential give few lines, elements of weak electro-potential give many lines, and that elements with a low polar number (1—3) show very intense lines, whilst those with a high polar number (above 5) show lines of weak intensity. The spectrum is thus not the result of a number of homogeneous atoms, but the average result of different atoms or atom species. Thus the elements with strong *E.M.F.* have few species of atoms, the electrons being arranged in a few definite positions, whilst elements of weak *E.M.F.* have many species, the electrons being arranged in a variety of systems. The paper contains also a spiral arrangement of the periodic system from which the new periodic table is derived (*A.*, 1918, ii, 306, 396).

CHEMICAL ABSTRACTS.

**Spectrum of Hydrogen Positive Rays.** G. P. THOMSON (*Phil. Mag.*, 1920, [vi], **40**, 240—247).—The positive ray spectrum of hydrogen has been examined under varying conditions in the discharge tube, whereby the proportion of atoms and molecules was varied over a wide range. The experiments show that the Balmer series is produced when positively charged hydrogen atoms pass through hydrogen as positive rays. The second spectrum is produced when positively charged hydrogen molecules pass through hydrogen as positive rays. The failure of Stark and Wilson to find the Döppler effect for the second spectrum of hydrogen is probably to be explained by the absence of molecules in the positive rays used. In certain circumstances a great change can be made in the nature of the positive rays given by a discharge tube by subjecting it to a magnetic field.

J. F. S.

**Krypton and Xenon.** J. N. COLLIE (*Proc. Roy. Soc.*, 1920, [A], **97**, 349—354).—A number of hitherto unmeasured lines have been observed in the spectra of xenon and krypton. The lines are observed with a fairly strong discharge, but still more are visible when a Leyden jar is placed in the circuit. It was found impossible to photograph the lines, which were therefore directly measured. In the case of xenon, 44 lines are recorded between  $\lambda\lambda$  7121 and 6036, and with krypton 35 lines between  $\lambda\lambda$  6768 and 5718 are measured. The lines are all of low intensity, but in the case of one experiment with xenon with a jar discharge the following brilliant lines were

seen:  $\lambda\lambda$  6880 (5), 6730 (5), 6669 (5), 6470 (7), 6318 (8), 6179 (8). It was observed that after passing a heavy current for some hours the xenon entirely disappeared and the tube became vacuous. This occurred with krypton and hydrogen, but with the difference that in the latter cases the gas was regained when the metal splashes were heated, whilst with xenon no gas could be recovered on heating the tube, electrodes, or splashes. The disappearance of the xenon occurs most readily with platinum electrodes, and aluminium and copper come next. No gas is evolved when the splashes are dissolved in acid or alkali, consequently there is no formation of a compound corresponding with a hydride, unless this, on treatment with alkali, forms an alkali xenate. J. F. S.

### Revision of the Series in the Spectrum of Barium.

F. A. SAUNDERS (*Astrophys. J.*, 1920, **51**, 23—36).—A study of photographs taken by A. S. King of vacuum furnace spectra leads to the revision and extension of the known spectrum of barium.

CHEMICAL ABSTRACTS.

**Character of the Absorption Spectra Produced by the Electric Furnace. II. The Zeeman Effect for Electric Furnace Spectra. III. Electric Furnace Spectra of Cobalt, Nickel, Barium, Strontium, and Calcium in the Region of Greater Wave-length.** ARTHUR S. KING (*Astrophys. J.*, 1920, **51**, 13—22, 107—120, 179—186).—I. By placing a plug of graphite in the middle of a vacuum tube furnace a continuous spectrum depending on the temperature was produced with which the pure absorption spectra of barium, calcium, cobalt, iron, and titanium were studied. Those lines which are most intense in emission spectra were not always the strongest in absorption spectra. The absorption at each temperature stage corresponded with the emission spectrum several hundred degrees lower. By placing the plug beyond the middle of the furnace mixed spectra were obtained which should help to explain stellar spectra containing both bright and dark lines. II. The Zeeman effect noted in spark spectra has been closely checked by a study of the vacuum furnace emission and absorption spectra of iron in a magnetic field. III. The infra-red spectra for cobalt, nickel, barium, strontium, and calcium are tabulated. The lines that appear in the arc spectra above a certain minimum intensity usually appear in the furnace spectra, but not always in the same relative strength. The rules that hold for the visible spectrum as to change in intensity of the lines with temperature change hold for the infra-red.

CHEMICAL ABSTRACTS.

### Absorption Spectra of the Nitric Esters of Glycerol.

ELLIOT QUINCY ADAMS (*J. Amer. Chem. Soc.*, 1920, **42**, 1321—1327).—A theoretical consideration of the work of Hepworth (T., 1919, **115**, 840). It is shown that in plotting absorption spectra the use of the logarithm of the specific or molecular extinction-coefficient should be avoided, since it tends to obscure the rela-

tionship between absorption and constitution. The designations  $\alpha$ - and  $\beta$ - applied by Will (A., 1908, i, 384) to the two mononitrates derived from glycerol should be interchanged. It is possible that the "glycidnitrat" described by Nef (A., 1905, i, 3) is glyceryl orthonitrate. The absorption spectra of the nitric esters of glycerol as given by Hepworth (*loc. cit.*) can be completely accounted for on the assumption that each nitrate radicle has an absorptive effect dependent on its location in the molecule, but independent of the presence or absence of other nitrate radicles. The absorptive effect of the nitrate radicle is about 1.5 times as great when it replaces the  $\beta$ -hydroxyl of glycerol as when it replaces an  $\alpha$ -hydroxyl group

J. F. S.

**Dissociation of Iodine Vapour and its Fluorescence.** ST. LANDAU and ED. STENZ (*Phil. Mag.*, 1920, [vi], 40, 189—197).—The fluorescence of iodine vapour at low pressure has been examined with the object of ascertaining the effect of temperature and dissociation on it. It is shown that raising the temperature does not produce as great an effect on the fluorescence of iodine vapour as has hitherto been thought. Fluorescence has been observed at temperatures above 800°. Dissociation destroys both the fluorescence and the resonance spectra. Thus the complicated vibrating system, corresponding with thousands of absorption lines in the visible part of the spectrum, is not inherent in the atom, but in the molecule. The structure of the atom should therefore be relatively simple. This idea is perfectly in accord with other facts obtained from a study of the fluorescence of vapours. It appears nearly certain that the absorption lines, which are so characteristic for diatomic iodine and so sensitive to the action of monochromatic light, do not belong to the absorption spectrum of monatomic iodine. J. F. S.

**Radiating Potentials of Nitrogen.** H. D. SMYTH (*Physical Rev.*, 1919, 14, 409—426).—The author has derived an equation for making accurate corrections for the distribution of velocities among the impacting electrons which are used to obtain radiating potentials. This correction applied to the results obtained on the radiating potentials of nitrogen has given the following values: at  $8.29 \pm 0.04$  volts a strong resonance, at 7.3 volts a doubtful resonance, at  $6.29 \pm 0.06$  volts strong resonance at low pressures. The first value is probably connected to the Lyman doublet wave-lengths 1492.8 and 1498.8 Å.U. by the relationship  $P \cdot D \cdot \times q = h \nu$ . The author finds some difficulty in identifying the other potentials accurately with nitrogen lines. On an assumption identifying the last resonance potential (that is, at 6.29 volts) with a line of wave-length from 2000 to 3000 Å.U. coming from neutral atoms, it is estimated that the upper limit for the heat of dissociation of the nitrogen mol. is 190,000 cal. per gram-mol.

CHEMICAL ABSTRACTS.

**The Relative Activity of Radium and the Uranium with which it is in Radioactive Equilibrium.** J. H. L. JOHNSTONE and B. B. BOLTWOOD (*Phil. Mag.*, 1920, [vi], 40, 50—67).—A re-

determination of the ratio of the  $\alpha$ -activity of uranium, in equilibrium with its disintegration products, to that of the uranium (UI and UII) alone gave 4.73, in good agreement with Boltwood's first value, 4.69. The comparison was made with very thin films of the material, and in the case of the mineral, which was a selected specimen of uraninite from Spruce Pine containing 73% of uranium, the result was corrected for loss of emanation, and for thorium (1.9%  $\text{ThO}_2$ ) present. The ratio of the  $\alpha$ -activity of the radium itself to the uranium in the mineral was found to be 0.488, as compared with the first value, 0.45, and is far lower than the value, 0.57, deduced from the two-thirds power of the range of the respective  $\alpha$ -rays emitted, if the transformations involved were simple and direct. However, the first ratio, 4.73, is in excellent agreement with the value so calculated on the experimental datum that the branch actinium series contributes 0.28 to it. The last corresponds with a proportion of 8% of the uranium forming actinium and 92% radium. Now the two schemes proposed by Soddy and Cranston (A., 1918, ii, 211) for the origin of the actinium series require a ratio 0.55 and 0.53, according as the branch occurs at UI or UII, instead of the experimental value 0.488 already cited, if the actinium branch is 8%. Or, for the experimental value to be accounted for, an actinium branch of 26 or 14% respectively is required. Various possibilities are discussed without clearing up the discrepancy (compare Hahn and Meitner, this vol., ii, 147). F. S.

**Resonance and Ionisation Potentials for Electrons in the Monatomic Gases, Argon, Neon and Helium.** H. C. RENTSCHLER (*Physical Rev.*, 1920, **14**, 503—515).—With special precautions for eliminating impurities from the electrodes the author, using two methods (that of Tate and one similar to Lenards' first method), determined the resonance and ionisation potentials for argon, neon, and helium. He found ionisation potentials for helium to be about 26 volts, for neon about 19.5 volts, and for argon about 17 volts. Resonance potentials were only observed for the case of argon at about 12 volts. The accuracy of the values found is not great, as no correction was made for the initial velocities of the electrons.

CHEMICAL ABSTRACTS.

**Ionisation and Resonance Potentials for Electrons in Vapours of Lead and Calcium.** F. L. MOHLER, PAUL D. FOOTE, and H. F. STIMSON (*Phil. Mag.*, 1920, [vi], **40**, 73—79).—The metal is boiled at low pressure in a tube containing a Wehnelt cathode surrounded by a cylindrical grid and a plate, a variable potential to accelerate the electrons being applied between the cathode and the grid, and a small retarding field between the grid and the plate. A sudden increase in the electron current leaving the cathode as the accelerating potential is increased shows when the ionisation point is reached. The "partial current," grid to plate, decreases when the electrons near the grid lose their velocity by inelastic collisions, as is the case when the velocity

exceeds the resonance potential. For lead, a mean value of 1.26 volts for the resonance potential and 7.93 volts for the ionisation potential was obtained, which, by the quantum relation, correspond with wave-lengths 9800 Å. and 1550 Å. For calcium, two resonance potentials, at 1.90 and 2.85 volts, were found, the first being more prominent, and an ionisation potential of 6.01 volts. These are associated with the wave-lengths 6572.78 Å. (1.877 volts), 4226.73 Å. (2.918 volts), and 2027.56 Å. (6.081 volts). F. S.

**Electrical Conductivity of Mixtures of Salts in the Fused and Solid States.** C. SANDONNINI (*Gazzetta*, 1920, 50, i, 289—321).—Using the arrangement devised by Kohlrausch, the author has measured the electrical conductivities of various binary mixtures of salts belonging to each of the three groups: (1) mixtures the components of which are miscible in the fused, and, maybe, also in the solid, state, but do not combine; (2) mixtures forming compounds decomposed on fusion; (3) mixtures forming one or more compounds stable in the fused condition. The systems examined were: (1)  $\text{PbCl}_2$ – $\text{PbBr}_2$ ,  $\text{AgCl}$ – $\text{AgBr}$ ,  $\text{NaNO}_3$ – $\text{KNO}_3$ ,  $\text{NaCl}$ – $\text{KCl}$ . (2)  $\text{AgCl}$ – $\text{TiCl}_4$ ,  $\text{NaCl}$ – $\text{CaCl}_2$ . (3)  $\text{AgNO}_3$ – $\text{TiNO}_3$ ,  $\text{KCl}$ – $\text{CaCl}_2$ ,  $\text{TiCl}_4$ – $\text{CdCl}_2$ ,  $\text{KCl}$ – $\text{CdCl}_2$ .

The conductivities of the fused mixtures are in all cases found to be lower than the values calculated from the law of mixtures. With certain pairs, the conductivity isotherms exhibit minima, this occurring principally when the components combine. Such minima do not, however, correspond always with the compounds formed, and with the system  $\text{NaCl}$ – $\text{CaCl}_2$  a minimum conductivity occurs at a temperature at which, according to thermal analysis, the compound formed by the two salts is completely dissociated, and at a composition far different from that of the compound.

From the values of the specific conductivity alone, certain deductions cannot be drawn, since variations of volume taking place during reciprocal dissolution of the two salts result in variation of the ionic concentrations. The author has therefore determined the densities of the following typical fused mixtures of salts:  $\text{NaNO}_3$ – $\text{KNO}_3$ ,  $\text{NaCl}$ – $\text{KCl}$ ,  $\text{NaCl}$ – $\text{CaCl}_2$ , and  $\text{KCl}$ – $\text{CaCl}_2$ . In these cases, the variation in specific gravity occurring during mixing is very small, even when the presence of complex molecules in the fused mass may be assumed.

The equivalent conductivities for these mixtures have been calculated, the changes in density being taken into account. With those pairs of salts for which compounds exist in the fused mass, the differences between the observed and calculated conductivities are certainly the more marked, but the isotherms in general exhibit no singular points corresponding with the compositions of the compounds, although with  $\text{KCl}$ – $\text{CaCl}_2$  this is approximately the case.

Conductivity measurements have also been made on the following solid mixtures:  $\text{PbCl}_2$ – $\text{PbBr}_2$ ,  $\text{AgCl}$ – $\text{AgBr}$ , and  $\text{AgCl}$ – $\text{TiCl}_4$ . The results obtained show that, when the solidified salt mixtures



consist of solid solutions which may be regarded as perfectly homogeneous, the phenomena encountered with mixtures of aqueous solutions or of fused salts having a common ion are repeated, the electrical conductivity being less than the calculated value. For the system  $\text{TlCl-AgCl}$ , the conductivity curve exhibits a maximum coincident with the eutectic concentration (compare Benrath, A., 1909, ii, 12; Benrath and Wainoff, A., 1911, ii, 847), whereas the formation of solid solutions being excluded in this system, the presence in the mass of a double salt should produce a diminution, and not an increase, in the conductivity. The probable cause of this increase lies in a diminution of the internal friction, which, for a given isotherm, will be the lower as the temperature approaches more nearly the melting point. T. H. P.

**The Rectifying Contact Galena-metal. Artificial Sensitisation and Different Remarks.** C. FLORISSON (*Compt. rend.*, 1920, 171, 106—108).—Artificial sensitisation produces the rectification *B* in specimens of galena having a slight original rectification *A*. Various methods of promoting this change were examined. The metal used for the contact is platinum. Heating in an atmosphere of nitrogen has, as a rule, no effect, although in a few cases the rectification *B* was produced. The action of air at high temperature not only did not produce the rectification *B*, but tended to destroy it in specimens where it was apparent. The action of pure dry sulphur dioxide was very irregular, but sulphur vapour in a current of nitrogen almost invariably caused marked sensitisation. Selenium was similar, but much less marked in its action. In all these cases where sensitisation occurred, a very thin, superficial layer was apparently produced, which probably contained more sulphur than lead sulphide, the sulphur being present either in combination or in solid solution. The presence of this layer in naturally occurring sensitive galenas is discussed. W. G.

**Anode Corrosion of Lead in Sodium Hydroxide Solutions.** O. W. BROWN, C. O. HENKE, and L. T. SMITH (*J. Physical Chem.*, 1920, 24, 367—378).—The corrosion of lead anodes during the electrolysis of solutions of sodium hydroxide of various concentrations has been examined at 20°, 60°, and 75°, using current strengths of various values and an *E.M.F.* of about 3 volts. It is shown that the amount of corrosion increases rapidly with increasing temperature; thus, using a solution of 152 grams of sodium hydroxide per litre, the amount of corrosion is 4·5% of the theoretical at 20°, 98·3% at 60°, and theoretical at 75°. At all temperatures, the corrosion increases with increasing concentration of sodium hydroxide to a maximum, which is reached at 152 grams per litre, and then falls, with a further increase in concentration. Thus at 60° the following fractions of the theoretical amount of corrosion are observed with the given concentrations: 35 grams/litre, 5·7%; 71 grams/litre, 49·3%; 110 grams/litre, 96·4%; 152 grams/litre, 98·3%; 192 grams/litre, 58·5%; 220 grams/litre,

61.5%; and 304 grams/litre, 37.7%. The current efficiency increases rapidly with increase of temperature; this is especially marked where the concentration is 152 grams/litre and the current density 4 amperes/sq. dcm. The discharge potentials and the total polarisation have been determined for various current densities at 75° for a solution containing 152 grams/litre. It is found that there is 100% corrosion when the bath tension is low (0.2—0.3 volt), and a low corrosion when the voltage is high, 3.2. The total polarisation increases from -0.179 volt with a current density 1.56 amperes/sq. dcm. to -2.484 volts with 4.22 amperes/sq. dcm. When the anode is corroding properly, the discharge potential is about 0.2 volt, but when it ceases corroding, the discharge potential rises to -1.317 volts.

J. F. S.

### **Ballo-electricity, Molecular Forces, and Electrical Forces.**

J. TRAUBE (*Ann. Physik*, 1920, [iv], **62**, 165—172. Compare Christiansen, A., 1919, ii, 385).—A theoretical paper in which the author considers the results of Christiansen's work. It is shown that the ballo-electric charge of solutions runs parallel with the surface tension; abalistic substances are shown to be without effect on the surface tension, whilst catabalistic and anabalistic substances have considerable influence on the surface tension of the solvent. In the case of homologous series of organic acids and bases, it is shown that there is a continuous increase in the surface tension and the ballo-electric charge of the solutions with increasing molecular weight. It is shown that the molecular forces and the forces of cohesion, like the chemical affinity, are electrical in origin.

J. F. S.

**Mobility of the Electrolytic Ions.** M. BORN (*Zeitsch. Physik.*, 1920, **1**, 221—249).—A mathematical paper. An expression is deduced for calculating the radii of the ions. The radii of the alkali metal ions and the halogen ions have been calculated to be somewhat less than  $10^{-8}$  cm. It is further shown that the magnitude of the radius increases with the atomic number of the atom from which the ion is formed, and, for the same atomic number, that the radius increases with the magnitude of the charge carried by the ion.

CHEMICAL ABSTRACTS.

**Magnetic Susceptibilities of Quartz, Tellurium, and some Holmium Compounds.** GILLIS WISTRAND (*Diss. Uppsala*, 1916, 56 pages).—Samples to be tested were fastened to a glass plate which could be moved in and out of a magnetic field produced by two Ruhmkorff coils. The effect of forces acting on the samples was determined by weighing. The sample was hung by a fine copper wire, 1 metre long, to the underside of the pan of a precision balance, the sample hanging free between the electromagnetic poles. Samples investigated were two clear quartz cylinders about 10 cm. long, and practically free from iron, a bar of tellurium about 4 cm. long, commercial samples of ferric hydroxide, manganese dioxide and manganese sulphide, and ferric oxide, made by

heating ferric hydroxide; holmium oxide was tested in three fractions, because of the varying presence of other rare metals; the nitrate and chloride were also investigated. Similar determinations for comparison were made on water in a thin glass tube. The author found the specific magnetic susceptibility ( $x_s$ ) of water corrected for air to be  $-0.7260 \times 10^{-6}$ , for quartz in vacuum  $-1.070 \times 10^{-6}$ , for tellurium  $-1.70 \times 10^{-6}$ , for ferric hydroxide  $123.8 \times 10^{-6}$ , for ferric oxide  $60.7 \times 10^{-6}$ , for manganese dioxide  $37.3 \times 10^{-6}$ , and  $64.80 \times 10^{-6}$  for manganese sulphide.  $x_s = +132.6 \times 10^{-6}$  and  $+172.0 \times 10^{-6}$  for holmium nitrate and chloride respectively, which gave 51.4 as the value of the "magneton" number of holmium.  $x_s = +243 \times 10^{-6}$  was the average of the three fractions of holmium oxide, the fractions giving 51.4, 50.7, and 51.5, respectively, as the magneton numbers.

#### CHEMICAL ABSTRACTS.

**Calorimetric Method for Standardising Thermometers by Electrical Energy.** THEODORE W. RICHARDS and SETSURO TAMARU (*J. Amer. Chem. Soc.*, 1920, **42**, 1374—1377).—Thermometers may be standardised by immersing them in a calorimeter containing a known amount of water at a measured temperature, and adding measured amounts of heat by allowing a known electric current of suitable voltage through a definite resistance to enter the liquid, thus adding a measured quantity of electrical energy. The rise of temperature can then be calculated and compared with the temperature registered by the thermometer. This method is capable of giving results of the greatest accuracy. As an example of the method, a measured quantity of electrical energy was added nine times in succession to a calorimeter (adiabatic) containing a Beckmann thermometer. The readings were  $2.0505^\circ$ ,  $2.5555^\circ$ ,  $3.0510^\circ$ ,  $3.5475^\circ$ ,  $4.0440^\circ$ ,  $4.5375^\circ$ ,  $5.0320^\circ$ ,  $5.5225^\circ$ , and  $6.0080^\circ$ . Allowing for the difference of specific heat of water, the error in the thermometer is found to be  $+0.0102^\circ$  between  $2.55$  and  $3.05$ , and so on. J. F. S.

**The Expansion of Saturated Vapours.** G. BRUHAT (*Compt. rend.*, 1920, **171**, 162—164).—A mathematical discussion of the subject. W. G.

**Specific Heat of Saturated Vapours and Entropy-temperature Diagrams of Fluids.** ALFRED W. PORTER (*Phil. Mag.*, 1920, [vi], **40**, 211—212).—The author discusses some points in a paper under the above title by Ewing (this vol., ii, 412). It is shown the specific heat of the saturated vapour in the case of sulphur dioxide can be positive, and that the inversion temperatures are  $97.5^\circ$  and  $114^\circ$ . The entropy of a liquid is not  $\int_0^T C_p \cdot dT/T$ , where  $C_p$  is the specific heat at constant pressure, even with the proviso that the value of  $C_p$  must be taken at saturation. The value of  $C_p$  must be replaced by  $K_w$ , the specific heat of saturated liquid. The difference between  $C_p$  and  $K_w$  is negligible at temperatures suffi-

ciently remote from the critical temperature, but it tends towards +infinity as the critical temperature is approached. The relation between the two quantities is  $K_w = C_p - T(\delta v / \delta T)_p \cdot dp/dT$ , or, in terms of the specific heat at constant volume ( $C_v$ ), it may be expressed  $K_w = C_v - T(\delta p / \delta T)_v / (\delta p / \delta T)_r \cdot ds/dT$ , where  $s$  is the specific volume of the liquid at saturation. The values of  $K_w$  for sulphur dioxide are given for the range  $-20^\circ$  to  $155.5^\circ$ , and it is shown that  $K_w$  is not a linear function of the temperature even in regions remote from the critical region.

J. F. S.

**Method of Suppressing the Correction of Temperature in the Determination of Melting-points.** MAURICE FRANCOIS (*Bull. Soc. chim.*, 1920, [iv], **27**, 528—536).—The apparatus used is a long-necked flask having two side-tubes, one near the bulb and the other being the continuation of the neck of the flask. These two side-tubes are joined by a vertical tube, which is continued upwards and expanded into a bulb. The flask and vertical tube are filled with oil to just above where the elongated neck joins the vertical tube. The material under examination is placed at the closed end of a long capillary tube, which is then bent back on itself. This tube is attached to the bulb of a thermometer, which is then placed in the vertical tube connected with the flask, the scale of the thermometer thus being in the oil. By this means a correction for exposed stem is avoided. A simple arrangement of mirrors is described by means of which it is possible to read the thermometer and observe the material in the melting-point tube simultaneously through one telescope.

W. G.

**Estimation of Impurities by means of the Melting-point Curve.** WALTER P. WHITE (*J. Physical Chem.*, 1920, **24**, 393—416).—A theoretical discussion, accompanied by practical examples of methods of determining melting points and the estimation of impurities from the melting-point curves. It is shown that freezing points are more accurately determined by immersing the thermometer in the substance than by the capillary tube method. If, in addition, the form of the freezing-point curve is observed, an indication of the amount of impurity present is obtained, which is independent of all previous knowledge or uncertainty as to the melting point of the pure substance and even of the absolute accuracy of the thermometer. If the determinations are a control of a purification process, there is also a saving of time and the avoidance of certain chances of error. Smallness of dimensions of the melting tube diminishes local temperature differences, and is very often a superior substitute of the stirring rod. It also economises both time and material. A small thermocouple or cell of several couples is very useful with small test samples. The complications, usually almost negligible, arising from specific heat, uneven temperature, and other causes are considered, and suitable experimental arrangements are suggested for removing them.

J. F. S.

**Reduced Transition and Freezing Points.** J. NARBUTT (*Physikal Zeitsch.*, 1920, **21**, 341—349).—A mathematical paper, in which a number of relationships between the transition temperatures and melting points of substances respectively are deduced. It is shown that at similar reduced temperatures the ratio between the transition affinity or the fusion affinity and the heat of transition or the heat of fusion of substances at the transition temperature or the melting point,  $\Theta$ , respectively is the same for all substances,  $A'_{\tau}/U'_{\Theta} = A''_{\tau}/U''_{\Theta}$ . The ratio between the transition or fusion affinity and the transition or fusion temperature,  $\Theta$ , for similar reduced temperatures is the same for all substances with the same entropy value,  $S_{\Theta}$ .  $A'_{\tau}/\Theta = A''_{\tau}/\Theta$ . A similar relationship exists between the heat of transition or the heat of fusion and the corresponding temperature,  $U'_{\tau}/\Theta = U''_{\tau}/\Theta$ . The heat of fusion or transition may be calculated from the vapour pressure of the supercooled liquid or solid substance, or that of the labile and stable modifications by means of the formula

$$U_{\Theta} = 2R\Theta\phi/(1 - \phi^2) \cdot \log_e p_2/p_1.$$

The vapour-pressure curves of a supercooled liquid may be deduced if the vapour-pressure curve of the solid is known or vice versa. The ratio of the vapour pressure of the supercooled liquid and solid or the labile and stable modifications of a substance at the same reduced temperature is the same for all substances,  $p_2'/p_1' = p_2''/p_1''$ . At similar reduced temperatures the relationship  $\sqrt[p_2'/p_1']{\Theta} = \sqrt[p_2''/p_1'']{\Theta}$  holds for supercooled and solid substances or for the labile and stable modifications of a substance. The formulæ have been applied to the known data for benzene, water, and the halogen derivatives of benzene, and shown to hold very exactly. J. F. S.

**Practical Method of Determining the Boiling Point, with Small Amounts of Substance.** VICTOR ARREGUINE (*Soc. Chim. Argent.*, **3**, 133 [reprint]).—The apparatus consists essentially of a small test-tube, 80—85 mm. long and 9 mm. in diameter, having a loose inner tube open at one end and a bulb at the other end, being about 5 mm. in diameter and 52—54 mm. long. This inner tube is first filled with mercury to within 1 mm. of the top, and the liquid under examination is added. This tube is inverted into mercury in the test-tube, which is then filled with glass beads and closed with a metal cap. The whole apparatus is placed against the bulb of a thermometer and slowly heated in a bath of a suitable liquid. The temperature is read on the thermometer, when the mercury is at the same level in the test-tube and the inner tube. Certain corrections, all very small in amount, must be made for the vapour pressure of mercury and for the error produced by excess of liquid in the inner tube. Formulæ are given for calculating these. The method is only applicable for liquids having boiling points below 210°. W. G.

**Spontaneous Evaporation.** HARRY B. WEISER and EVERETT E. PORTER (*J. Physical Chem.*, 1920, **24**, 333—341).—The present paper records the results of a repetition of some of Babington's

experiments (*Proc. Roy. Soc.*, 1859, **10**, 132) on the spontaneous evaporation of solutions. In this paper it was stated that solutions of potassium ferrocyanide, potassium tartrate, copper sulphate, and potassium chlorate evaporated more rapidly than pure water under the same conditions. A number of experiments have been made with solutions of these substances of various concentrations, and the rate of evaporation determined. It is shown that to obtain reproducible results the containers must be scrupulously clean, and that they must be slowly rotated on a revolving platform. Crystallisation must all take place on the base of the dish, and there must be no creeping. It is shown that in all cases, even with saturated solutions, the evaporation is slower than with pure water. Taking the precautions mentioned, this method may be used for obtaining a fairly accurate measurement of the relative lowering of the vapour pressure of various substances. A number of comparison experiments on the evaporation of solutions of sulphuric acid and chromium trioxide indicate that the latter exists in dilute solution chiefly as dichromic acid, as was pointed out by Ostwald from other considerations.

J. F. S.

**Vapour Pressures of certain Substances: Chloropicrin, Cyanogen Bromide, Methylchloroarsine, Phenylchloroarsine, Diphenylchloroarsine, and Arsenic Trichloride.** G. P. BAXTER, F. K. BEZZENBERGER, and C. H. WILSON (*J. Amer. Chem. Soc.*, 1920, **42**, 1386—1393).—The vapour pressures of the substances named in the title have been determined at a series of temperatures by the air current method, except in the case of arsenic trichloride at higher temperatures, where the static method was employed. The vapour pressure in all the cases can be expressed by a formula of the type  $\log p = A + B/(273 + t)$ ; values of  $A$  and  $B$  have been deduced in each case. The following equations and values actually measured have been obtained: chloropicrin,  $\log p = 8.2424 - 2045.1/273 + t$ ;  $-20^\circ$ , 1.50 mm.;  $-19^\circ$ , 1.70 mm.;  $-18^\circ$ , 1.90 mm.;  $0^\circ$ , 5.71 mm.;  $10^\circ$ , 10.37 mm.;  $15^\circ$ , 13.82 mm.;  $20^\circ$ , 18.31 mm.;  $25^\circ$ , 23.81 mm.;  $30^\circ$ , 31.10 mm.;  $35^\circ$ , 40.14 mm.; cyanogen bromide,  $\log p = 10.3282 - 2457.5/273 + t$ ;  $-17.3^\circ$ , 5.9 mm.;  $-15.5^\circ$ , 6.3 mm.;  $0^\circ$ , 21.2 mm.;  $15^\circ$ , 63.3 mm.;  $25^\circ$ , 119.5 mm.;  $35^\circ$ , 223.5 mm.; methylchloroarsine,  $\log p = 8.6944 - 2281.7/273 + t$ ;  $-17^\circ$ , 0.60 mm.;  $-16.8^\circ$ , 0.61 mm.;  $-15^\circ$ , 0.71 mm.;  $0^\circ$ , 2.17 mm.;  $15^\circ$ , 5.91 mm.;  $25^\circ$ , 10.90 mm.;  $35^\circ$ , 19.33 mm.; phenylchloroarsine,  $\log p = 9.150 - 3164/273 + t$ ;  $0^\circ$ , 0.004 mm.;  $15^\circ$ , 0.014 mm.;  $25^\circ$ , 0.035 mm.;  $35^\circ$ , 0.076 mm.;  $45^\circ$ , 0.159 mm.; diphenylchloroarsine,  $\log p = 7.8930 - 3288/273 + t$ ;  $25^\circ$ , 0.0003 mm.;  $45^\circ$ , 0.0039 mm.;  $55^\circ$ , 0.0065 mm.;  $65^\circ$ , 0.0148 mm.;  $75^\circ$ , 0.0282 mm.; arsenic trichloride,  $\log p = 7.5183 - 1720/241.2 + t$ ;  $0^\circ$ , 2.44 mm.;  $25^\circ$ , 11.65 mm.;  $35^\circ$ , 19.53 mm.;  $50^\circ$ , 40.90 mm.;  $60^\circ$ , 64 mm.;  $70^\circ$ , 97 mm.;  $80^\circ$ , 145 mm.;  $90^\circ$ , 211 mm.;  $100^\circ$ , 301 mm. The following heats of vaporisation have been calculated by means of the Clausius-Clapeyron formula,

$$L = T \cdot dp/dt(V_{\text{gas}} - V_{\text{liq.-solid}}).$$

Chloropicrin,  $35^{\circ}$ , 6.77;  $0^{\circ}$ , 7.10; cyanogen bromide,  $35^{\circ}$ , 8.08;  $0^{\circ}$ , 8.60; arsenic trichloride,  $100^{\circ}$ , 6.86;  $50^{\circ}$ , 7.29;  $0^{\circ}$ , 7.42. An accuracy of a few per cent is claimed for the numerical values.

J. F. S.

**Determination of the Last of the Three Functions which Define the Equation of State of Ethyl Ether.** E. ARIÈS (*Compt. rend.*, 1920, 171, 154—156).—The values of the functions  $x$  and  $\Phi$ , which define the equation of state of ethyl ether (compare this vol., i, 418), have been determined, and it is necessary only to determine the values of  $a$  for the equations  $v_1 = RT_c x(a + y_1)/8P_c \Phi$  and  $v_2 = RT_c x(a + y_2)/8P_c \Phi$ . Using the values obtained experimentally by Young for the liquid state, it is possible to calculate the numerical values of  $a$  for each  $10^{\circ}$  and to find an expression which represents this function:

$$a = a_c + (1 - \tau)^2/10^{\Theta},$$

where  $\Theta = (A + B\tau + C\tau^2 + D\tau^3)/0.0073688$  and the value of  $a_c$  is given by  $v_c = RT_c(a_c + 2)/8P_c$  which gives  $a_c = 0.09809$ .

The results calculated from these formulæ are in close agreement with those found experimentally by Young.

W. G.

**Equation of State.** M. P. APPLEBEY and D. L. CHAPMAN (*Phil. Mag.*, 1920, [vi], 40, 197—200).—The mean kinetic energy of translation of a molecule can no longer be assumed to be proportional to the temperature, and consequently the dynamical definition of temperature must be abandoned. From this point of view the authors deduce a new equation of state. They start with the assumption "that in a closed space which contains a large number of similar molecules the ratio of the number of molecules per unit volume whose potential energy is  $A$  to the number of molecules per unit volume whose potential energy is zero is given by the expression  $e^{-A/kt}$ , in which  $k$  is the gas constant for a single molecule and  $t$  the thermodynamic temperature." The final form of the equation deduced is  $[Pb'/(e^{Pb'/kt} - 1)] + Pb'/2 = \frac{2}{3}mV^2/2$ , in which  $m$  is the mass of a single molecule of the gas and  $b'$  the volume of fluid displaced by the molecule.

J. F. S.

**Equation of Condition.** C. DIETERICI (*Ann. Physik*, 1920, [iv], 62, 75—94).—A theoretical paper, in which the author considers the pressure isothermals obtained by Young (A., 1899, ii, 633) for isopentane and by Amagat (A., 1893, ii, 152) for carbon dioxide. It is shown that the difference between the ideal saturation work,  $A_{id} = RT \log_e v_2/v_1$ , and the actual work,  $A_s = p_s(v_2 - v_1)$ , is given by the expression  $(a - RTv_k)(S_1 - S_2)$ , in which  $S_1$  and  $S_2$  are the saturation densities and  $a$  a constant which is determined by the critical data alone.

J. F. S.

**Correspondence of Substances in the Solid State.** FÉLIX MICHAUD (*Compt. rend.*, 1920, 171, 241—243).—The law of corresponding states has been generalised by making coincide certain

homologous points instead of the critical points (compare Curie, *Arch. Sci. phys. nat.*, 1891, 26), and taking as specific units the co-ordinates of these points. There exists such a point in the solid region which is particularly useful. It has been shown that the specific heat,  $C$ , tends towards zero as the absolute temperature,  $T$ , approaches zero. Consequently,  $C/T=0$  when  $T=0$ , and it also tends towards zero for  $T=\infty$ , and in consequence it must pass necessarily through a maximum, and it is this point, where the temperature is  $T_m$ , that is taken as a centre of correspondence. Thus the law of Dulong and Petit is only exact when the substances are taken in their corresponding states, as just defined, that is, at the absolute temperatures proportional to the temperatures  $T_m$ . It further results that the atomic entropies, at temperatures proportional to the temperatures  $T_m$ , are equal. These facts are demonstrated in the cases of aluminium, silver, copper, lead, and zinc.

W. G.

**Calorimetric Procedure for Determining the Heat of Slow Reactions. I. Analysis of Partially Concurrent Heat Effects.** FREDERICK BARRY (*J. Amer. Chem. Soc.*, 1920, 42, 1295—1308).—A theoretical paper in which the method of extrapolating, from a time-temperature change curve of two concurrent reactions, the temperature change of a single process is developed. In the case of the inversion of sucrose by acid, the heat changes are two: (1) heat of solution of the solid sucrose in the acid solution, and (2) heat of inversion. This case is considered as well as the cases where there is concurrent heat reaction in the same sense, that is, both exothermic or both endothermic, and concurrent heat reactions in opposite senses, as in the case of sucrose and dilute acid. Equations are developed whereby extrapolation of the desired heat change may be made from the experimental curves.

J. F. S.

**Thermochemistry of Hydrocarbons according to P. W. Zubov's Data.** W. SWIETOSLAWSKI (*J. Amer. Chem. Soc.*, 1920, 42, 1312—1321. Compare this vol., ii, 470).—A theoretical paper in which the values recalculated by the author from Zubov's data (*loc. cit.*) are critically examined. By analysis of the equations for the combustion of hydrocarbons, the terms  $(y + w - 2z) = Y$  and  $(x + w - z - w) = X$  are obtained, which correspond respectively with the heats of combustion of the linkings C-C and C-H;  $y$  is the heat of formation of the atomic linking C-C,  $x$  that of C-H,  $2w$  the heat of formation of the molecule  $O_2$ ,  $4z$  that of  $CO_2$ , and  $2w$  that of  $H_2O$ . The terms  $X$  and  $Y$  are termed the thermochemical characteristics of the C-C and C-H linkings respectively. These characteristics have remarkably constant values in the case of *n*-hexane, *n*-octane, *n*-decane, cyclohexane, and naphthalene. Hence, if the molecule of naphthalene contains the double bond C=C, the heat of formation of this double bond is exactly the same as that of two single bonds, C-C. The value of  $X$  and  $Y$  for



methane and ethane are exactly the same as in the cases mentioned above. The following values of the thermochemical characteristics  $X$  and  $Y$  and of the homologous difference  $Z$  are  $X = -53.72$  cal.,  $Y = -52.25$  cal.,  $Z = 2X + Y = -157.77$  cal. In spite of the proved constancy of  $X$  and  $Y$  in five saturated, one polymethylene, and one aromatic hydrocarbon, they are shown to vary in other hydrocarbons. It is definitely established that the heat of formation of the C-C linking increases with the increase of the number of carbon atoms in the polymethylene hydrocarbons, and that the heat of formation of the same linking is increased by the replacement of a hydrogen atom by a methyl or a  $n$ -propyl group. The increase in  $Y$  is not considerable. In the case of the polymethylene hydrocarbons, it varies between  $-0.5$  and  $+0.5$  in the series *cyclopentane*, *cyclohexane*, *cycloheptane*. It varies within the limits  $-0.8$  and  $+1.7$  when one, two, or three methyl groups are introduced in the molecule of the polymethylene hydrocarbons. The analysis of the data on unsaturated hydrocarbons shows the important difference  $2(y - y_2)$  between the heat of formation of two single linkings, C-C, and that of the double one, C=C. This difference, due to the change of constitution of the hydrocarbon examined, varies within the very large limits,  $+8.0$  cal. to  $+1.0$  cal. In special cases it is possible that  $2(y - y_2)$  can be equal to zero, for example, in the case of naphthalene. J. F. S.

**Static Friction. II.** W. B. HARDY (*Phil. Mag.*, 1920, [vi], 40, 201—210. Compare *ibid.*, 1919, [vi], 38, 32).—The relationship between chemical constitution and the lubrication of bismuth has been examined at  $11$ — $14^\circ$  by measuring the static friction between a burnished bismuth surface and bismuth slider,  $70.5$  grams weight and  $25.5$  mm. radius of curvature, lubricated by a large number of pure organic substances, which included thirteen alcohols, ten acids, two ketones, six esters, nine hydrocarbons, all of these of the aliphatic series, and forty-five cyclic compounds. It is shown that static friction is a function of the molecular weight of the lubricant, and in a simple series of chain compounds, such as fatty acids, alcohols, or paraffins, a good lubricant will be found if the series is taken high enough. It is by no means a simple function; the friction, for example, rises sharply in moving from chloroform to carbon tetrachloride, and from phenol to quinol and catechol. The influence of molecular weight is overshadowed by constitution. A linear relationship is found in the series benzene, naphthalene, anthracene, the paraffins, and ammonia-propylamine. In the aliphatic acids and alcohols, the linear relation to molecular weight is disturbed by the weighting of the chain at one end by the  $-\text{CO}_2\text{H}$  and  $-\text{OH}$  groups respectively. In a simple chemical series, lubrication and viscosity change in much the same way with molecular weight, but there is no fundamental relation between viscosity and lubrication. The curves for acids, alcohols, and paraffins show no break where, with increasing molecular weight, the lubricant becomes a solid at the temperature of observation,

as is shown by the pairs, benzene-naphthalene, menthone-menthol, thymol-carvacrol. The upward trend of the first part of the curve for the aliphatic alcohols is in agreement with the fact that methyl alcohol is abnormal in some of its physical properties. In their qualities as lubricants of bismuth, ring compounds are the converse of chain compounds; thus, the effect of a double bond is to decrease the lubricating value of the former and increase that of the latter. On the other hand, the presence of unsaturated atoms increases the lubricating qualities of chain compounds, whether it be the double-bonded oxygen of ketones or acids, or carbon of olefines and alcohols, but this rule is departed from in the case of acids when the chain becomes much elongated. When a ring and chain are joined, as in butylxylene, the product is a better lubricant than either constituent. When the atoms are disposed with complete symmetry about a carbon atom, the compound is a very bad lubricant, as is seen in the case of carbon tetrachloride and pentaerythritol,  $C(CH_2 \cdot OH)_4$ . In the ring compounds, the replacement of hydrogen decreases lubricating power in the case of N,  $:O$ , or  $-CO_2H$ , and increases it in the case of other groups in the order  $C_2H_5 < CH_3 < OH$ . The effect of a second group of the same or of a different kind is to decrease the effect of the first, and the simpler the group the more effective it is. Esters occupy an unexpected position. The aliphatic esters are much worse lubricants than their related acids or alcohols. Hydroxy-acids have a remarkably good lubricating power in the aliphatic series, but this is entirely lost in cyclic compounds. Generally, it is noted that no cyclic compound is a good lubricant. It is also shown that the better a lubricant is, the more strongly is it adsorbed by a metal surface.

J. F. S.

**Adsorption by Charcoal. I. Relation of Service Time to Adsorption and Absorption.** H. H. LOWRY and G. A. HULETT (*J. Amer. Chem. Soc.*, 1920, **42**, 1393—1408).—The adsorption of nitrogen, carbon dioxide, and water by a large number of different varieties of charcoal has been studied. It is shown that no relationship exists between the length of time the charcoal has been in use and the adsorption for gases, such as nitrogen and carbon dioxide. Differences in the method of preparation of the charcoal change the adsorptive capacity by as much as 100%. Nitrogen and carbon dioxide adsorbed by charcoal may be regarded as a condensed layer one molecule thick. Measurements of the isothermal adsorption of water at  $25^\circ$  show that there is no adsorption in the strict sense of the term, but that the water is held in the capillary tubes, that is, it is absorbed. Using Anderson's formula (A., 1914, ii, 632) connecting the radius of a capillary with vapour pressure, the mean diameters of the capillaries of four specimens of charcoal have been calculated, and are found to vary from  $2.8 \times 10^{-7}$  cm. to  $9.2 \times 10^{-7}$  cm. The maximum diameter of any of the charcoal examined was  $1.3 \times 10^{-6}$  cm. By means of the same formula and the absorption isothermals of

water, the surface of the charcoal is found to vary from 160 sq. metres to 436 sq. metres per gram. The variation of surface is not always accompanied by a corresponding variation in adsorptive capacity. This makes the conception of elementary spaces, as postulated by Langmuir, a necessity. There is no relationship between the volume of the capillaries and the time of use of the charcoal. The same is also true for the saturation point and the retentivity of the charcoal.

J. F. S.

**Adsorption by Charcoal. II. Relation of Oxygen to Charcoal.** H. H. LOWRY and G. A. HULETT (*J. Amer. Chem. Soc.*, 1920, **42**, 1408—1419. Compare preceding abstract).—The adsorption of oxygen by charcoal has been examined with several varieties of charcoal. In the case of this gas, the behaviour is shown to be anomalous, due to the coupling of two phenomena, adsorption and surface combination. Charcoal has been heated in a furnace up to 1200° out of contact with oxygen-containing materials, and the evolved gases collected and analysed. The results point to the formation on the charcoal surface of a carbon-oxygen complex, which is essentially a stable solid oxide of carbon, at ordinary temperatures. This complex decomposes on heating into carbon monoxide and carbon dioxide, and can thus be considered to be an intermediate compound in the combustion of charcoal. This is supported by the views of Armstrong (A., 1904, ii, 948) and by the experimental work of Rhead and Wheeler (T., 1912, **101**, 831; **103**, 461), and by Langmuir (A., 1915, ii, 467). The amount of oxygen thus found to be combined in charcoal has been found to vary in two samples from 1.71% and 3.75% of the initial weight of the charcoal.

J. F. S.

**Solubility. II. Solubility Ratios of Salts in Strong Homöionic Solvents.** J. N. BRÖNSTED (*J. Amer. Chem. Soc.*, 1920, **42**, 1448—1454. Compare this vol., ii, 294).—The solubility of potassium chloride, bromide, iodide, nitrate, chlorate, and iodate has been determined at 20° in solutions of potassium hydroxide of concentrations varying between 4.71*N* and 15.02*N*. The solubility of the haloids and the chlorate steadily decreases with increasing concentration of the hydroxide, that of the nitrate remains constant at the higher concentrations of hydroxide after decreasing with increasing hydroxide concentration, whilst the iodate decreases to an hydroxide concentration 11.10*N*, and then increases to 14.85*N*. The results are considered in the light of the views put forward in an earlier paper (*loc. cit.*). It is found that, taking the salts in pairs, the ratio of the solubility products is constant over a considerable range of hydroxide concentration, except in the case of the nitrate-chlorate ratio. The results indicate that the nitrate, chlorate, and iodate ions are equally hydrated. The salts investigated fall into groups: (1) the haloids and (2) the oxygen salts. The salts in either group exhibit similar behaviour as solutes, and are similarly hydrated and equally acted

on by electric forces in the solvent over a wide range of concentrations.

J. F. S.

**Hypophosphorous Acid. I. Its Ionisation Equilibria.** ALEC DUNCAN MITCHELL (T., 1920, 117, 957—963).

**Polarity and Ionisation from the Point of View of the Lewis Theory of Valency.** WENDELL M. LATIMER and WORTH H. RODEBUSH (*J. Amer. Chem. Soc.*, 1920, 42, 1419—1433).—A theoretical paper in which the conceptions of polarity and the ionisation of polar and non-polar compounds are considered on the basis of Lewis's valency hypothesis (A., 1916, ii, 310). Salts of elements which are not polar are ionised in solution by reacting with the solvent molecules or other molecules. The properties of an ionising solvent depend on the existence of moderately strong intermolecular fields. The dielectric constant is a measure of this type of polarity, but it has no significance with regard to highly polar compounds.

J. F. S.

**The Crystal Lattice.** A. REIS (*Zeitsch. Physik.*, 1920, 1, 204—220).—A method based on a pure geometrical conception of the space lattice is put forward to answer the questions of the nature of the existence of molecules and radicles in the crystal lattice. Application of this method to chemical compounds shows that a fundamental difference exists between the space lattice of salts and compounds not exhibiting a salt-like character. For chemical and crystallographic problems the method has many applications. It is shown that the distances between atoms in molecules and radicle ions are appreciably smaller than those between molecules. Classification of the kinds of lattices has been found to produce a homogeneous picture of the relation which exists between chemical constitution and cohesion forces, whilst the differences between these classes are readily shown by a consideration of the compressibility, hardness, and thermal expansion. The cohesion forces in all states of aggregation, as well as the association forces in liquids, are essentially the same, and result from pure electrostatic influences of the molecule. Those optical properties of salts which correspond with the mutual linking of ions are associated with the state of aggregation, whilst all other optical properties are independent of it. Both the heat of transition of polymorphous modifications and the heat of sublimation are distinctly less for molecular lattices than for ion lattices. In ion lattices, and only in these, the molecular union is raised and displaced by the lattice union.

CHEMICAL ABSTRACTS.

**Arrangement of Atoms in Crystals.** W. LAWRENCE BRAGG (*Phil. Mag.*, 1920, [vi], 40, 169—189).—An examination of the distances between neighbouring atoms in a crystal leads to an empirical relation determining these distances. The distance between the centres of two atoms may be expressed as the sum

of two constants characteristic of the atoms. The arrangement of the atoms in a crystalline structure may therefore be pictured as that of an assemblage of spheres of appropriate diameters, each sphere being held in place by contact with its neighbours. This empirical law is summarised in a curve, in which the constants for a number of elements are plotted against the atomic numbers. The curve is periodic, and resembles Lothar Meyer's curve of atomic volumes. Each atom occupies a constant space in any crystalline structure of which it forms part. The space occupied by the alkali metals and the metals of the alkaline earths is greatest, that occupied by the halogens and electronegative elements least. The accuracy of the relationship is discussed. Variations of the order of 10% between the calculated and observed distances occur, so that the law is only approximately true. Nevertheless, it is of considerable assistance in the analysis of the more complex crystal structures, since the conception of the atoms as an assemblage of spheres of known diameters packed tightly together limits the number of possible arrangements which have to be tried in interpreting the diffraction of X-rays by the crystal. The physical significance of the relation is examined with reference to Langmuir's theory of atomic structure. From this point of view, it follows that two electronegative atoms are situated close together in a crystalline structure because they share electrons, and the spheres representing them are therefore assigned small diameters. On the other hand, an electropositive element does not share the electrons in its outer shell with neighbouring atoms, and is therefore situated at a distance from other atoms, so that it appears to occupy a greater space in the structure. It is shown that the relationship is less accurate when applied to the crystals of metals, which, on Langmuir's theory, consist of an assemblage of positive ions held together by electrons which have no fixed positions in the structure. From the distance between electronegative atoms holding electrons in common, an estimate is made of the diameter of the outer electron shell of the inert gases. The following values are given: neon 1.30 Å., argon 2.05 Å., krypton 2.35 Å., and xenon 2.70 Å. The atomic diameter of some thirty-eight elements is given, and the distance between the atoms in a large number of crystals.

J. F. S.

**Rate of Change of Distribution of Particles in a Colloidal System.** A. WESTGREN (*Arkiv. Mat. Astron. Fysik*, 1918, 13, No. 14, 18 pp.).—An experimental verification of Smoluchowski's formula for the rate of change of concentration of particles in a colloidal system,  $\Delta^{-2} = 2\nu P$ , in which  $P = (4/\alpha\pi)$

$$\int_{\sqrt{\alpha}}^{\infty} dR \int_0^{\sqrt{\alpha}} dr \int_{-1}^{+1} (e^{-R^2 - r^2 + 2RT\xi} / \sqrt{1 - \xi^2}) R r d\xi,$$

$\alpha = a^2/4Dt$ , and, according to Einstein,  $D = (RT/N)(1/6\pi\eta r)$ . This formula permits a determination of Avogadro's constant which leads to  $N = 60.9 \times 10^{22}$ , with a probable error of 5%.

CHEMICAL ABSTRACTS.

**Distribution of Acetic Acid between Water and Charcoal.**

ALWYN PICKLES (*Chem. News*, 1920, **121**, 49).—When acetic acid solutions are treated with charcoal, a large proportion of the acid is rapidly removed, but several hours are required for complete equilibrium to be attained. Relatively more acid is removed from dilute solutions, and the concentration of the acid in mols. per c.c. of charcoal varies with the kind of charcoal and its state of division. An increase of temperature over a long period, so that the surface and interior effects are complete, reduces the acid concentration of the charcoal, but over a short period increases it, owing to the acceleration of the still incomplete interior effect. Animal charcoal is an exception, since it removes the acid almost entirely by adsorption. In applying the distribution equation,  $\frac{C_n \text{ Charcoal}}{C \text{ Water}} = K$ , the values of  $n$  giving the most consistent values

for  $K$  ranged from 1.76 to 2.6. The value for  $n$  (2.35) in Thorpe's "Dictionary of Applied Chemistry," vol. ii. (colloids), thus appears to be an average value.

C. A. M.

**Equilibrium between Chlorine, Plumbous Chloride, and Plumbic Chloride in Aqueous Solution.**

ERNEST W. WESCOTT (*J. Amer. Chem. Soc.*, 1920, **42**, 1335—1349).—The equilibrium between solid plumbous chloride and chlorine in hydrochloric acid has been investigated with acid of concentrations down to the point where lead dioxide separates as a solid phase. The results show that the complex chloroplumbic acid has the composition  $\text{HPbCl}_5$ , for with a given chlorine pressure the quantity of this complex acid present in equilibrium with solid plumbous chloride was found to be proportional to the first power of the chloride-ion concentration. The hydrogen-ion concentration, which would not be involved in the equilibrium if the ionisation of the substances was complete, was found to have a small secondary effect, probably owing to an influence on the ionisation of the chloroplumbic acid. The equilibrium constant corresponding with the expression  $(\text{PbCl}_5')/(\text{Cl}')$ .  $p_{\text{Cl}}$  is given by the expression  $K' = 0.055 + 0.07c_{\text{H}}$ , the concentrations being expressed in mols. per 1000 grams of water, the partial pressure of chlorine being given in atmospheres and the ionisations of hydrochloric acid and chloroplumbic acid being assumed equal. The equilibrium constant of the reaction  $\text{PbCl}_2(s) + \text{Cl}_2(g) + 2\text{H}_2\text{O} = \text{PbO}_2(s) + 4\text{H}^+ + 4\text{Cl}'$ , as given by the expression  $K = (\text{H}^+)^4 \cdot (\text{Cl}')^4 / p_{\text{Cl}}$ , was found to be  $2.4 \times 10^{-8}$ , under the assumption that the ionisation of the hydrochloric acid and the chloroplumbic acid is complete. From these equilibrium constants and from other data found in the literature, the values of the decrease of free energy at  $25^\circ$  were calculated for the case that the concentrations of all dissolved substances are molecular, except that of chlorine, the partial pressure of which is one atmosphere, and were found to be those expressed by the following free energy equations:  $\text{PbCl}_2(s) + \text{Cl}_2(g) + \text{Cl}' = \text{PbCl}_5' - 6590$  joules,  $\text{PbCl}_2(s) + 2\text{H}_2\text{O} + \text{Cl}_2(g) = \text{PbO}_2(s) + 4\text{H}^+ + 4\text{Cl}' - 43,500$  joules, and  $\text{Pb}(s) + \text{O}_2(g) = \text{PbO}_2(s) + 219,000$  joules.

J. F. S.

**The Kinetic Theory of Gases in the Light of the Theory of Relativity.** RUDOLF MEWES (*Zeitsch. Sauerstoff. Stickstoff. Ind.*, 1920, 12, 33—34; from *Chem. Zentr.*, 1920, iii, 70—71).—A connexion has not yet been established between the kinetic theory of gases or its laws and the theory of relativity developed by Lorentz, Gerber, Einstein, and Minkowski. The author's previous experiments and new calculations open the possibility of developing a dynamic theory of gases and vapours on the basis of the general law of action of mass.

H. W.

**Magnitude of the Atom.** A. LANDÉ (*Zeitsch. Physik.*, 1920, 1, 191—197).—A theoretical paper on the sphere of influence of the electrons. It is stated that the radius of the second electron ring of atoms having an atomic number in the neighbourhood of 10 is approximately  $0.35 \times 10^{-8}$  cm. Values are given for the lattice constant,  $\delta = 2r_+ + 2r_-$ , for a number of alkali haloids. Here  $r_+$  and  $r_-$  are the radii of the positive alkali- and the negative halogen-ions (or better of their spheres of influence). The following first approximations have been deduced for the diameters of the spheres of influence of a number of ions:

Na <sub>+</sub> .	K <sub>+</sub> .	Rb <sub>+</sub> .	Cs <sub>+</sub> .	F <sub>-</sub> .	Cl <sub>-</sub> .	Br <sub>-</sub> .	I <sub>-</sub> .
$2r \times 10^8 = 2.2$	2.9	3.3	3.2	2.4	3.3	3.6	4.1

It is shown that  $r_+/r_- = 0.68$  for eight electrons and  $= 0.51$  for four electrons. That the value for the ratio for eight electrons is smaller than that calculated from the series of numbers given above, is explained on the ground that in the lattice the large halogen-ion spheres are more compressed than in the smaller alkali-ion spheres.

CHEMICAL ABSTRACTS.

**New Periodic Relationship between the Atomic Weights of the Chemical Elements. II. Law of Mirror Image Remainders.** KARL FEHRLE (*Physikal. Zeitsch.*, 1920, 21, 382—385. Compare this vol., ii, 303).—In a previous communication (*loc. cit.*) the author determined the difference between the ideal atomic weight and the actual atomic weight for the elements with atomic numbers 1—37. In the present paper the elements with atomic numbers 38—74 have been treated in the same way. The author now plots the differences as ordinates against the atomic numbers as abscissæ, and obtains an irregular curve which can be divided by a line at atomic number 37 into two halves which are exact mirror images of one another, that is, where a maximum is found in the first half of the curve, a minimum occurs in the same relative position in the second half of the curve and vice versa. It is shown that by means of this relationship doubtful atomic weight values may be checked and corrected.

J. F. S.

**General Isotopy.** A. VAN DEN BROEK (*Physikal. Zeitsch.*, 1920, 21, 337—340).—A theoretical paper, in which the general relationships of isotopes are discussed. It is shown that if the periodic

system were a system of only two series, for example,  $3 + 4n$  and  $4n$ , without nucleus electrons, then atomic weight  $= 2Z$  and  $2Z + 1$  respectively, and all atomic weights would be whole numbers ( $Z$  is the atomic number). That this is not so is conditioned in the first place by the existence of at least two other series,  $1 + 4n$  and  $2 + 4n$ , the atoms of which are less common. A table is drawn up of the whole of the elements on the basis of the above-named four series, and a system of isotopes on the  $4\alpha/2\beta$  hypothesis is given for the elements with atomic numbers 29 to 35.

J. F. S.

**Nuclear Constitution of Atoms.** Sir E. RUTHERFORD (*Proc. Roy. Soc.*, 1920, [A], **97**, 374—400).—Bakerian lecture. A general discussion of previously published work on the constitution of the lighter atoms. Structures are put forward for carbon, nitrogen, and oxygen atoms.

J. F. S.

**A Force, apparently due to Mass, Acting on an Electron, and the Non-identity of Isotopes in Spectra and other Properties.** WILLIAM D. HARKINS and LESTER ARONBERG (*J. Amer. Chem. Soc.*, 1920, **42**, 1328—1335).—A theoretical paper, in which the nature of isotopes is discussed. It is shown that isotopes may be distinguished by their spectra, and that there must be some difference, although small, between the other properties of isotopes.

J. F. S.

**Glass to Metal Joints.** E. C. McKELVY and C. S. TAYLOR (*J. Amer. Chem. Soc.*, 1920, **42**, 1364—1377).—A résumé of the various metal glass joints described in the literature is given, and this is followed by a description of the method of making trustworthy joints between metal and glass. Two types of joint are described: (a) soldered joints, (b) fused joints. The first type of joint has only been used for joining tubes. A length of glass tube chosen so that it will fit easily inside the metal tube, is roughened for a length of 15—20 mm. and then coated with platinum by covering it with a suspension of platinum chloride in oil of lavender, and then burning off carefully in a bunsen flame. The metal tube is carefully coated with tin, solder, or lead. Using a slightly acid solution of zinc chloride as soldering flux, the metal tube is heated so that the tin is molten and the hot glass tube inserted and the whole allowed to cool slowly. Fused joints are made between metal and glass by means of the Kraus flux (equal weights of zinc oxide, borax, and powdered soda glass fused together). The metal tube is covered on its interior with a thin layer of the flux, the glass tube is flared out to a flat ring of a width equal to three times the thickness of the glass wall, and while hot pressed into the flux-lined metal tube. Fusion is completed by heating the outside of the metal tube in such a way that the glass is kept cool enough to prevent deformation. An account is given of the various types of apparatus for which these joints are applicable.

J. F. S.



**Equipment for Drying Ovens.** C. W. FOULK (*J. Amer. Chem. Soc.*, 1920, **42**, 1454—1455).—The drying space in ovens is considerably augmented by removing the door and placing a number (three or four) drawers on each shelf, so that the whole oven space is filled with these easily removed drawers. The bottoms of the drawers are made of metal gauze, and the ease of use makes the back of the oven as convenient of access as the front. J. F. S.

**Washing Bottles in Gas Works Laboratory Practice.** H. J. HALLSTONE (*Gas World*, 1920, **72**, 376).—The inlet tube reaches to the bottom of the bottle and terminates in an upturned jet. Around it is a spiral tube, its lower end fitting over and being supported by the jet. An aperture should be left between the lower end of the spiral tube and the point of the jet, and for this purpose the lower end of the spiral tube is flattened, thus preventing the jet from completely closing the tube. In operation, the bottle is filled level with the top of the spiral with the solution, and the gas passed through it. The bubbles issue from the jet and ascend through the spiral carrying "plugs" of the solution with them, thus keeping the gas in contact with the liquid for a longer time. At the top of the spiral the gas passes out and the "plugs" of liquid fall back. Circulation of the liquid is thus made practically constant and the washing efficient. CHEMICAL ABSTRACTS.

**Apparatus for Ultrafiltration.** RICHARD GANS (*Ann. Physik*, 1920, [iv], **62**, 327—330).—An apparatus for rapid ultra-filtration is described. The principle of the present apparatus is the same as that of Bechhold (*A.*, 1908, ii, 24, 823), but the construction is much simpler. Collodion filters are conveniently prepared by treating 12.5 grams of guncotton with sufficient absolute alcohol to moisten it, and then making the volume up to 500 c.c. with ether. A little of the solution is poured evenly on a glass plate, and when the ether has evaporated it is plunged into water to remove the filter from the glass. The filter is then washed in running water, and may be preserved in water containing a little chloroform or formalin. A more rapid filter is obtained when equal volumes of alcohol and ether are used in the preparation. The permeability of a filter can be varied by the addition of glacial acetic acid, but the permeability does not depend entirely on the quantity of acetic acid used, but also on the time which has elapsed between its formation and its use. J. F. S.

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### Inorganic Chemistry.

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**Solubility of Iodine in Hydriodic, Hydrobromic, and Hydrochloric Acids, and Formation of the Corresponding Polyhalogenated Acids. I.** E. OLIVERI-MANDALÀ and A. ANGENICA (*Gazzetta*, 1920, **50**, i, 273—281).—The saturated

aqueous solution of iodine at 25° contains 0.0334% of iodine, or 0.00131 mol. per litre. The solubilities of iodine in solutions of various concentrations of hydriodic, hydrobromic, and hydrochloric acids have also been determined. It is found that the solubility of iodine in the halogen hydracid is equal to that in the solution of the corresponding potassium salt at the same concentration; the solubility of the iodine is hence specific to the halogen ion, and is independent of the nature of the positive ion of the halogen compound. The freezing points of hydriodic and hydrobromic acid solutions are unaltered by dissolution of iodine in these solutions. Further, if the existence of trihalogenated acids in dilute solution be assumed, it is found that the degree of dissociation of hydriodic acid in solutions of 0.1—0.3*N*-concentration is equal to that of the acid,  $\text{HI}_3$ ; the same holds for  $\text{HBr}$  and  $\text{HBr}_3$ . T. H. P.

#### Distribution of Ozone in the Direct Current Corona.

ERIC K. RIDEAL and JAKOB KUNZ (*J. Physical Chem.*, 1920, **24**, 379—392).—The formation of ozone by various methods is considered theoretically in the light of the various radiation hypotheses, and the conclusion is drawn that molecular species of a given type may be activated to varying degrees by a given radiation. The distribution of ozone in a direct-current corona is experimentally examined. The corona was produced in a brass tube with quartz ends, a platinum wire being suspended centrally down the tube and connected to the positive pole of a current of 16,500 volts, whilst the brass tube is earthed. Oxygen was slowly passed through the corona, and samples were withdrawn at various points and analysed. To control the analyses, an optical analysis was also carried out by means of a beam of ultraviolet light and a photoelectric cell. It is shown that the distribution of ozone in the corona varies very notably with the sign of the discharge, the negative corona producing higher concentrations than the positive corona. The average yield of ozone obtained was 0.045 gram/coulomb at the negative corona and 0.024 gram/coulomb at the positive corona. The distribution of ozone in a direct-current positive corona differs in a marked manner from that in a negative corona. The ultraviolet light emission from the corona exceeds that of the visible light, and in the corona itself the ratio of ultraviolet light to visible light is exceedingly high. J. F. S.

#### Sulphur Dioxide as a Source of Volcanic Sulphur.

JACOB PAPISH (*Proc. Indiana Acad. Sci.*, 1918, 170—171).—Sulphur dioxide is reduced to sulphur by methane at elevated temperature. The author suggests that sulphur occurring in volcanic regions may, in part, be formed by reduction of sulphur dioxide by methane, carbon monoxide, or hydrogen, all of which occur in volcanic exhalations.

CHEMICAL ABSTRACTS.

**Freezing-point Solubility Curve for Sulphur and Dichlorodiethyl Sulphide.** J. A. WILKINSON, CHRIST NEILSON, and H. M. WYLDE (*J. Amer. Chem. Soc.*, 1920, **42**, 1377—1382).—The solubility of rhombic sulphur, monoclinic sulphur, and

amorphous sulphur has been determined in  $\beta\beta'$ -dichlorodiethyl sulphide over the temperature range  $13.82$ – $128^\circ$ , and the solubility-freezing-point curves constructed. The solubility of rhombic and monoclinic sulphur is the same at all temperatures. Below  $78^\circ$ , the solid phase which crystallises is rhombic sulphur, whilst above that temperature monoclinic sulphur separates. The solubility of amorphous sulphur is less than  $0.14\%$  at temperatures below  $120^\circ$ . Saturated solutions of sulphur in dichlorodiethyl sulphide contain  $7.6\%$  of sulphur at  $80^\circ$ ,  $11.3\%$  at  $90^\circ$ ,  $17.5\%$  at  $100^\circ$ , and  $21.0\%$  at  $104^\circ$ .  
J. F. S.

**The System Ammonia-Water.** S. POSTMA (*Rec. trav. chim.*, 1920, **39**, 515–536).—The melting-point curve of the system ammonia-water shows the existence of two hydrates,  $\text{NH}_3 \cdot \text{H}_2\text{O}$  and  $2\text{NH}_3 \cdot \text{H}_2\text{O}$ , having m. p.'s  $-79.0^\circ$  and  $-78.8^\circ$  respectively. The boiling-point curves do not give any indication of the existence of these compounds.

The vapour-pressure curve of ammonia was determined, and is represented by the formula  $\log p = 7.2379 - 1282.86/T$ , from which the heat of vaporisation is calculated as  $5864$  cal. The vapour-pressure curves of mixtures of ammonia and water were constructed, and also the curve of sublimation of solid ammonia. W. G.

**Oxidation of Arsenious Anhydride in Alkaline Medium in the Presence of Ferrous Sulphate.** G. GIRE (*Compt. rend.*, 1920, **171**, 174–176).—The absorption of oxygen by a solution of arsenious oxide and ferrous sulphate in the presence of sodium hydroxide varies with the amount of alkali present. The volume of oxygen absorbed at first diminishes as the amount of alkali increases, reaching a minimum when the alkali is slightly in excess of that required to form the arsenite,  $\text{Na}_2\text{As}_2\text{O}_4$ . It then increases to a constant maximum, when the amount of alkali present is slightly in excess of that required to form the arsenite,  $\text{Na}_4\text{As}_2\text{O}_5$ . If the amount of alkali present is kept constant, the oxygen absorbed is proportional to the amount of iron present, but is always in excess of that required to oxidise the ferrous salt to the ferric state.  
W. G.

**Charcoal before the War. III.** WILDER D. BANCROFT (*J. Physical Chem.*, 1920, **24**, 342–366. Compare this vol., ii, 429).—A further discussion of the properties of charcoal. In the present paper, the oxidation of charcoal from various sources by various reagents is considered.  
J. F. S.

**The Action of Extremely Finely Divided Gases.** C ZENGHELIS (*Compt. rend.*, 1920, **171**, 167–170. Compare this vol., ii, 363).—A more detailed study of the reduction of carbon dioxide in the presence of water by hydrogen in a very finely divided state shows that the action steadily diminishes in velocity with the time. Although it takes place to some extent in the dark, it is markedly accelerated by sunlight, and still more so by

ultraviolet rays. In all cases, the formaldehyde first produced rapidly undergoes polymerisation. The reduction of carbon dioxide by hydrogen takes place slowly with both gases in solution in water without any passage of the hydrogen through a porous vessel.

W. G.

**Some Sources of Helium in the British Empire.** J. C. McLENNAN (*Bull.* No. 31, Dept. of Mines, Canada).—An account of the natural gases of Canada, British Columbia, New Zealand, New Brunswick, and England, which contain helium. The radioactivity and helium content are tabulated, and methods of estimation are described. [Compare T., 1920, 117, 923; this vol., ii, 488, 508.] J. F. S.

**Application of the Laue Diagram to the Determination of the Structure of Calc Spar.** ERNST SCHIEBOLD (*Leipziger Abh.*, 1919, 36, 65—213; from *Chem. Zentr.*, 1920, iii, 123).—The investigation was undertaken with the object of elucidating suitable methods of determining indices and of applying the Laue diagram to a useful means of determining structure. The systematic procedure recommended gives results confirmatory of Bragg's structure model when applied to sodium chloride. The structure deduced for calc spar permits a satisfactory explanation of the cleavage relationships from Bragg's model. H. W.

**The Constituents Formed by Reciprocal Penetration of Zinc and Copper at a Temperature at which these Two Metals and all their Alloys are in the Solid State.** H. WEISS (*Compt. rend.*, 1920, 171, 108—111).—When zinc and copper were heated in close contact at 400° for two days, the following constituents were found in the contact layer: pure zinc or its solid solution,  $\eta$ ; the constituent  $\epsilon$  to a thickness of about 0.2 mm.; the constituent  $\gamma$ , thickness about 1 mm.; a very thin zone of the constituent  $\beta$ ; and copper or its solid solution,  $\alpha$ . If the duration of heating was increased to ten days, the thickness of the zones  $\epsilon$  and  $\gamma$  increased without appreciable alteration of the zone  $\beta$ . W. G.

**System Zinc Oxide, Phosphoric Oxide, and Water at 25° and 37°.** N. E. EBERLY, C. V. GROSS, and W. S. CROWELL (*J. Amer. Chem. Soc.*, 1920, 42, 1433—1439).—The equilibrium between zinc oxide, phosphoric oxide, and water has been determined at 25° and 37° over a long range of concentrations, and the equilibrium curves have been constructed. At 25° the solid phases,  $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{ZnHPO}_4 \cdot 3\text{H}_2\text{O}$ , and  $\text{Zn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ , separate, whilst at 37° an additional solid phase,  $\text{ZnHPO}_4 \cdot \text{H}_2\text{O}$ , is obtained. The tetrahydrate of normal zinc orthophosphate may be prepared by saturating a 50% solution of phosphoric oxide in water with zinc oxide at the boiling point. The water lost by evaporation is replaced and the mixture cooled in ice. About 10 volumes

of ice-cold water are added, and the solution vigorously stirred and poured through a filter into a large porcelain dish. The dish and its contents are heated on a water-bath with stirring, when a large quantity of shining plates of the tetrahydrate separate.  $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  crystallises in shining, orthorhombic plates;  $\text{ZnHPO}_4 \cdot 3\text{H}_2\text{O}$  forms sticky, thread-like crystals which agglomerate into cotton-wool-like masses;  $\text{ZnHPO}_4 \cdot \text{H}_2\text{O}$  forms small, hard, transparent needles, which, since the extinction is oblique to the long axis, are probably triclinic;  $\text{Zn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  forms large, transparent, triclinic rhombohedra.

J. F. S.

**New Method of Preparing Tripotassium Lead Hydrogen Octafluoride.** FRANK C. MATHERS (*J. Amer. Chem. Soc.*, 1920, **42**, 1309—1311. Compare Clark, A., 1919, ii, 513).—Lead peroxide is readily attacked by 96% hydrofluoric acid, and a yield of 62% of lead tetrafluoride obtained. On dilution of the solution, the tetrafluoride is speedily hydrolysed, but this may be largely prevented by the addition of a little potassium or ammonium fluoride before dilution. Tripotassium lead hydrogen octafluoride,  $3\text{KF} \cdot \text{HF} \cdot \text{PbF}_4$ , is best prepared by fusing a mixture of equal weights of potassium hydrogen fluoride and lead peroxide in a platinum dish at  $200^\circ$ . The fluoride is melted and the dioxide slowly added, and the heating continued until the mass becomes pasty. After cooling, the mass is moistened with concentrated hydrofluoric acid, stirred with a carbon rod, and heated at  $225^\circ$  for several hours; after repeating the heating several times, the mass becomes practically white and contains 80—86% of the octafluoride. Pure crystals were obtained by digesting the crude residue with concentrated hydrofluoric acid, filtering, and crystallising. The pure salt is very easily hydrolysed, but the presence of a small excess of potassium fluoride retards the hydrolysis to a marked degree. The action of heat on the octafluoride does not give enough fluorine for the odour to be recognised, although the platinum dish was etched.

J. F. S.

**Crystal Structure of Ferromagnetic Metals.** ALBERT W. HULL (*Physical Rev.*, 1919, **14**, 540—541).—Since the atoms of ferromagnetic materials are, in general, ferromagnetic only when in pure metallic condition and between definite limits of temperature, and the relative spacing of the atoms is apparently essential, it might have been anticipated that ferromagnetic metals would have the same crystal structure. That this is not the case is shown by the data on the type of lattice and the distance between atoms of chromium, iron, cobalt, and nickel (compare *ibid.*, 1917, **10**, 661). Nickel has the same crystal structure as copper, whilst cobalt appears in two forms, one like copper and one like magnesium. Neither is like iron. Chromium, which is not ferromagnetic, has a centred cubic arrangement, like iron. It is evident, therefore, that ferromagnetism does not depend on any particular arrangement of atoms. It is much more likely that it depends on

the distance between the atoms, which would explain the fact that this property is lost when the temperature is increased beyond a definite value.

CHEMICAL ABSTRACTS.

**Catalytic Action of Copper Salts on the Oxidation of Ferrous Compounds by Air.** L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1920, **171**, 65—69).—Copper salts exert a marked catalytic effect on ferrous salts, favouring their oxidation in air. This effect is noticeable at extreme dilutions (1 in 100,000,000), and is sensitive to the least change in the reaction of the medium. It is apparently independent of the degree of ionisation of the mixture of copper and ferrous salts, but is most marked with ferrous salts of weak acids, being apparently related to their degree of hydrolytic dissociation.

W. G.

**The Precipitation of Tin by Iron.** N. BOUMAN (*Rec. trav. chim.*, 1920, **39**, 537—541).—By the addition of a solution of stannous chloride, the potential of iron in a solution of ferrous chloride becomes less negative, so that it is then less electronegative than tin; consequently it is no longer in the state to precipitate tin from its solution. This result is discussed on the electronic theory, and a satisfactory explanation given. At the same time, it is shown that reduced iron will precipitate tin from its solution if boiled with a slightly acid solution of stannous chloride.

W. G.

**Zirconium.** J. W. MARDEN and M. N. RICH (*J. Ind. Eng. Chem.*, 1920, **12**, 651—656).—Fairly pure (99·8%) zirconium oxide may be prepared from zircite by decomposing the mineral with sulphuric acid, precipitating the zirconium as basic sulphate, and igniting the precipitate. Good yields are also obtained by fusing zircite with sodium carbonate and hydroxide and precipitating zirconium oxide by means of sulphur dioxide, and by a method in which the zirconium is precipitated as phosphate. Potassium zirconium fluoride may be prepared in pure condition by dissolving zirconium dioxide in hydrofluoric acid, treating the solution with the calculated amount of potassium carbonate, and recrystallising the salt three times. Its solubility in water varies greatly with the temperature, 100 c.c. dissolving 25·0 grams at 100°, 15·0 grams at 18°, and 0·78 gram at 0°. The pure metal may be prepared from this salt or from the oxide. The coherent metal may be obtained by aluminothermic reduction, by heating the amorphous product, and (in admixture with carbide) by reducing zirconium oxide with carbon. The amorphous variety is obtained by reducing potassium zirconium fluoride by means of sodium or aluminium in an exhausted iron tube or a vacuum furnace. The coherent metal is much less chemically active than the amorphous variety, and, unlike the latter, is insoluble in all acids except aqua regia and hydrofluoric acid. A study of different analytical methods showed that zirconium is incompletely precipitated as fluoride, and that it is only quantitatively precipitated by peroxide when the concentra-

tion of the latter in the solution is high. The precipitation as phosphate is best effected in the presence of 10% of sulphuric acid, hydrogen peroxide being added to retain the titanium in solution. The quantity to be precipitated should not exceed 0.05—1 gram in 200 c.c., and the liquid should be heated to boiling point and allowed to remain after the addition of an excess of disodium hydrogen phosphate. In the case of solutions containing 10 to 20% of sulphuric acid, an excess of 50% of ammonium phosphate should be added. [See also *J. Soc. Chem. Ind.*, 1920, September.]

C. A. M.

**Thorium and Uranium Content of Certain Minerals; the Gradual Transformation of Thorium-B—Thorium-C.** STEFAN MEYER (*Sitzungsber. Akad. Wiss. Wien*, **128**, [2a], 897—908; from *Chem. Zentr.*, 1920, iii, 75).—The estimation of thorium or uranium in uranium ores containing very little thorium, or in thorium ores with a very small uranium content, cannot be effected by the usual methods; it is, however, relatively easy to estimate minimal amounts of uranium by the proportional radium content, and of thorium through its active precipitates. In a specimen of monazite sand, the ratio of thorium to uranium was 83:1, an extreme value, which is not commonly observed. A specimen of Joachimsthal pitchblende contained  $6.64 \times 10^{-5}$  grams of thorium isotopes (thorium + ionium) for 1 gram of uranium, or  $3.33 \times 10^{-7}$  grams of radium. The thorium content of a crystalline Morogoro uranium mineral, the uranium content of which was already known, was estimated in the following manner. The amount of thorium-B obtained under definite conditions from a known weight of the mineral was compared with the amount produced under identical conditions from a mineral of known thorium content. The Morogoro mineral was thus found to contain 0.53% of thorium and 74.5% of uranium. The amount of thorium is so great that the equivalent of the thorium-ionium from the mineral can scarcely be distinguished from that of thorium itself. In an appendix, the author gives tables showing the effect of differing exposure in thorium emanation on the activity of active thorium precipitates. H. W.

**Crystalline Structure of Antimony.** R. W. JAMES and NORMAN TUNSTALL (*Phil. Mag.*, 1920, [vi], **40**, 233—239).—The crystal structure of antimony has been determined for antimony by means of an X-ray spectrometer, using a bulb with a palladium anti-cathode. The glancing angles for first-order spectra were as follows: (100),  $5^{\circ}27'$ ; (110),  $7^{\circ}24'$ ; ( $\bar{1}\bar{1}0$ ),  $7^{\circ}50'$ ; (111),  $4^{\circ}26'$ ; and ( $\bar{1}\bar{1}\bar{1}$ ),  $19^{\circ}14'$ . The intensities and the small glancing angle indicate that the underlying structure is a face-centred lattice, and that the unit rhomb contains eight atoms. The structure, as in the case of the diamond, consists of two interpenetrating face-centred lattices. The arrangement of the lattices can be seen, as follows. "Suppose for one of the lattices, diagonals are drawn parallel to the trigonal axis for each of the eight equal rhombo-



hedral cells into which the unit lattice may be divided. From considerations of symmetry, it is clear that the atoms of the second lattice must lie in these diagonals. If they lay at the unoccupied corners of the first lattice, the structure would become a simple rhombohedral one. This does not accord with the observed facts, but if the atoms of the second lattice are all displaced from these corners along the diagonals in the same direction by a distance equal to 0.074 of the length of the diagonal of one of the small cells, all the observed facts are explainable." J. F. S.

**Revision of the Atomic Weight of Bismuth. Analysis of Bismuth Chloride.** O. HÖNIGSCHMID and L. BIRCKENBACH (*Sitzungsber. Akad. Wiss. München*, 1920, 83—86; from *Chem. Zentr.*, 1920, iii, 122).—With the object of discovering possible isotopes of bismuth, the authors have analysed and investigated bismuth chloride and bromide, using the methods of Richards and his co-workers. The ratio  $\text{BiCl}_3:3\text{AgCl}$  was determined gravimetrically, and the ratio  $\text{BiCl}_3:3\text{Ag}$  by gravimetric titration with the aid of the nephelometer. The first series gave the value  $\text{Bi}=209.024$ , whilst the second set indicated  $\text{Bi}=209.027$ ; the mean, 209.026, is regarded as the present most probable value for the atomic weight of bismuth, and is a unit higher than that previously adopted. H. W.

**[Salts with High Ammonia Content.]** WALTER PETERS (*Ber.*, 1920, 53, [B], 1143).—The formation of ammines containing more than six molecules of ammonia (Ephraim and Moser, this vol., ii, 378) has previously been observed by the author, who has obtained platinum double salts with 9, 12, 15, or 18 molecules (compare Peters, A., 1910, ii, 114). H. W.

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### Mineralogical Chemistry.

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**Pulverulent Mineral [Fluorite] from Dorgali, Sardinia.**

ENRICO CLERICI (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 309—312).—This mineral, which is shown by its physical and chemical properties to be fluorite, exhibits thermoluminescence, even under carbon tetrachloride or acetone, and emits radiations capable of influencing photographic plates and of penetrating glass, mica, or gelatin, but not aluminium or black paper. This phenomenon may be due to the presence of traces of rare earths.

T. H. P.

**Plumbiferous Barytes from Shibukuro, Japan.**

RYŌICHI ŌHASHI (*Min. Mag.*, 1920, **19**, 73—76).—The mineral is deposited

by a hot spring, the water of which has the following composition in parts per thousand: H 0.07500, K 0.02491, Na 0.04415,  $\text{NH}_4$  0.00011, Ca 0.04870, Mg 0.01483, Fe 0.24846, Al 0.09622, Cl 2.69729,  $\text{H}_2\text{SO}_4$  0.42034,  $\text{SO}_4$  0.93776,  $\text{HBO}_2$  0.04244,  $\text{H}_2\text{SiO}_3$  0.37022; total, 5.02043;  $D^{19}$  1.0030. In the rock fissures and at the orifice where the temperature is nearly  $100^\circ$ , the deposit consists of ordinary barytes, but in the stream of hot water, with a temperature of  $40$ – $50^\circ$ , the crystalline deposit consists of plumbiferous barytes of the variety known as "hokutolite" (so named from the occurrence in the hot spring at Hokuto, in Formosa), together with sulphur, siliceous sinter, ferric oxide, realgar, and orpiment. It has the composition:

	BaO.	PbO.	$\text{SO}_3$ .	Fe.	Ign.	Total.
I.	59.96	4.67	32.77	—	—	97.40
II.	48.95	17.78	32.24	trace	0.60	99.57

corresponding with  $\text{A}_1\text{B}_{14}$  and  $\text{A}_1\text{B}_3$ , whilst for the mineral from Hokuto the composition ranges from  $\text{A}_1\text{B}_3$  to  $\text{A}_3\text{B}_5$  (where A=anglesite, B=barytes). The optical characters are intermediate between those of anglesite and barytes, and this supports the suggestion that the mineral is an isomorphous mixture. The barytes, whether containing lead or not, is radioactive, ranging from 0.32 to  $1.37 \times 10^{-10}$  curie units per gram of mineral. It also exhibits a self-luminescent effect, and when heated glows brilliantly (thermoluminescence).

L. J. S.

**Analyses of Dolomites.** C. L. HARDING, J. B. SHUMAKER, and A. W. ROTHROCK (*Chem. News*, 1920, **121**, 50–52).—Twenty analyses are given of specimens (crystals and rocks) labelled as dolomite; some proved to be ordinary limestone or calcite, and in one case a sandstone (compare this vol., ii, 118).

L. J. S.

**Lead Minerals from the Wreck of a Fire-ship.** ARTHUR RUSSELL (*Min. Mag.*, 1920, **19**, 64–68).—Cavernous masses of metallic lead mixed with charcoal were taken up in 1846 from beneath the partly fused lead pump of a fire-ship which was wrecked in Falmouth Harbour in the year 1780. They show small crystals of cotunnite ( $\text{PbCl}_2$ ), anglesite ( $\text{PbSO}_4$ ), leadhillite ( $4\text{PbO} \cdot \text{SO}_3 \cdot 2\text{CO}_2 \cdot \text{H}_2\text{O}$ ), and galena ( $\text{PbS}$ ). These were evidently formed by the action of sea-water on the lead.

L. J. S.

**Nephelite from Parco Chigi, Ariccia, Rome.** FRANCESCO STELLA STARRABBA (*Riv. Min. Crist. Ital.*, 1917, **48**, 52–64).—Material eminently suitable for analysis was supplied by clear, colourless crystals from a volcanic bomb consisting mainly of biotite. The refractive indices,  $\omega_a = 1.5417$ ,  $\epsilon_{Na} = 1.5382$ , etc., are at the higher limit for nephelite.  $D^{21}$  2.65.

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	CaO.	MgO.	$\text{Na}_2\text{O}$ .	$\text{K}_2\text{O}$ .	Cl.	$\text{SO}_3$ .	$\text{H}_2\text{O}$ .	Total.
42.57	33.58	0.68	2.15	0.06	14.48	5.73	trace	0.29	0.15	99.69

This gives the ratios  $\text{SiO}_2:\text{Al}_2\text{O}_3:\text{RO}=2.12:1:1.01$ . Deducting  $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$  and  $(\text{Ca},\text{Mg})\text{Al}_2\text{Si}_2\text{O}_8$ , and plotting the remaining  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Na}_2\text{O}$  on a triangular diagram, all recent analyses of nephelite fall on a line between the limits  $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$  and  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}$ , the present analysis being nearest to the latter. The differences in composition of nephelite are explained by mixtures of these four molecules, but which of them exerts an influence on the variations in refractive indices could not be determined.

L. J. S.

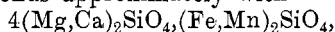
**So-called Hydrocastorite from Elba.** PROBO COMUCCI (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 264—267).—Doubts have been cast by Manasse (A., 1902, ii, 90) and D'Achiardi (A., 1906, ii, 555) on Grattarola's view that hydrocastorite represents a definite mineral species (A., 1878, 119). The author's analysis of Grattarola's mineral gives the percentage composition:

$\text{H}_2\text{O}$ .	$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{Na}_2\text{O}+\text{K}_2\text{O}$ (by difference).
16.60	56.63	18.73	0.42	5.56	2.04

From these results and from the physical properties of the mineral the author draws the conclusion that it represents, not a definite mineral, but either a mixture of certain secondary minerals of uncertain and varying composition or, sometimes, simply somewhat impure stilbite

T. H. P.

**Olivine from Etna.** FRANCESCO STELLA STARRABBA (*Mem. Classe Sci. R. Accad. Zelanti, Acireale*, 1917, [iii], **9**, 41—65).—Small crystals occurring in tuffs are separated according to colour and crystal-habit into: I, olivine of a clear green colour and fairly transparent,  $D\ 3.42$ ,  $\gamma_N\ 1.707$ ; II, hyalosideritic olivine of a dark brownish-green colour and almost transparent,  $D\ 3.56$ ,  $\gamma_{Na}\ 1.7303$ . Analysis I corresponds approximately with



and II with  $7(\text{Mg},\text{Ca})_2\text{SiO}_4, 3(\text{Fe},\text{Mn})_2\text{SiO}_4$ . The frequent presence of ferric oxide in volcanic olivine is commented on.

	$\text{SiO}_2$ .	$\text{TiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{Cr}_2\text{O}_3$ .	$\text{FeO}$ .
I.	37.97	0.05	1.01	5.24	—	14.26
II.	37.43	0.57	0.71	5.82	trace	19.34
	$(\text{Co},\text{Ni})\text{O}$ .	$\text{MnO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{H}_2\text{O} ?$	Total.
I.	—	0.32	0.54	40.71	0.34	100.44
II.	0.11	0.64	1.00	34.43	0.14	100.19

L. J. S.

**"Titanolivine" from the Ala Valley, Piedmont.** F ZAMBONINI (*Bull. Soc. franç. Min.*, 1919, **42**, 250—279).—"Titanolivine" is of frequent occurrence in the serpentine rocks of the Alps, and its presence accounts for the wide diffusion of titanium in these rocks. Dark reddish-brown crystals found at several places in the Ala valley agree in their crystallographic

constants ( $a : b : c = 1.0735 : 1.5.667$ ,  $\beta = 89^{\circ}59\frac{1}{2}'$ ) and optical orientation with clinohumite, but they differ chemically from this in containing some titanium and also hydroxyl in place of fluorine. Analysis gave:

SiO <sub>2</sub> .	TiO <sub>2</sub> .	PbO.	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	GIO.	FeO.	MnO.	NiO.	MgO.
36.83	1.92	0.14	0.42	0.07	1.30	4.90	0.28	0.07	51.53
CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	$\frac{H_2O}{(<110^{\circ})}$ .		$\frac{H_2O}{(>110^{\circ})}$ .		F.	Total.	
0.03	0.09	0.03	0.05		2.99		0.03	100.68	

corresponding with the ratios  $SiO_2 + TiO_2 : RO : H_2O (+ F) = 1 : 2.23 : 0.26$ , and with the formula  $4Mg_2SiO_4, Mg(OH)_2$ . The mineral is decomposed by hydrochloric acid. Water is expelled only at a high temperature. Glucinum has been previously detected in a mineral of this group by Jannasch and Locke (A., 1894, ii, 459), but lead is unusual. The earlier analyses of "titanolivine" by A. Damour (1855 and 1879) and G. Anelli (A., 1905, ii, 176) agree with the clinohumite formula only when it is assumed that titanium replaces magnesium, and they are probably at fault. The name "titanolivine" being thus inadmissible for this mineral, *titanhydroclinohumite* is suggested as an alternative. L. J. S.

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### Analytical Chemistry.

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**Method of Stating Analytical Results.** A. THIEL (*Chem. Zeit.*, 1920, **44**, 525—526. Compare this vol., ii, 187).—The author suggests a nomenclature for equivalent or molecular quantities, for example, "norm" (symbol  $gN$ ) for gram-equivalent, "mol" ( $gM$ ) for gram-molecule, etc. W. P. S.

**The Significance of the "Specific Refraction" for Analytical Chemistry.** N. SCHOORL (*Rec. trav. chim.*, 1920, **39**, 594—599).—The specific refraction,  $(n-1)/d$ , may serve as a confirmatory measurement for the identification of an unknown organic compound, but its application is somewhat limited. W. G.

**Fluoremetry. Quantitative Analysis by Comparative Fluorescence.** L. J. DESHA (*J. Amer. Chem. Soc.*, 1920, **42**, 1350—1363).—A new method of micro-analysis is described, of the same order of sensitiveness as colorimetry and nephelometry, which should prove generally applicable to the estimation of minute quantities of the considerable number of substances which are either fluorescent themselves or may be rendered so by the addition of a suitable reagent. Ultraviolet rays from a quartz mercury

lamp are filtered from most of the visible radiation and used to excite fluorescence in solutions of such substances contained in the comparison cylinders of the Kober nephelometer. The intensity of the fluorescent light thus produced, as observed in the eyepiece of the instrument, is equalised in the usual manner by altering the heights of the exposed columns. For sufficiently dilute solutions, the curves obtained by plotting the scale readings against concentrations are quite regular. These calibration curves are drawn for solutions containing 0.5—2 mg. per litre of quinine sulphate in *N*-sulphuric acid, and for solutions of 2—4 mg. per litre of aniline iodoeosin in *N*/10-alkali. Such a curve differs from that of inverse proportionality (the colorimetric curve) much more than from one drawn according to the nephelometric formula. Some peculiarities of the latter are indicated, and it is shown that when two constants are used (one for solutions stronger than the standard and the other for those more dilute), the values corresponding with the fluoremetric readings may be taken from the nephelometric curve with an average error of 1%. J. F. S.

**A Gas Analysis Apparatus Accurate to 0.001% mainly designed for Respiratory Exchange Work.** AUGUST KROGH (*Biochem. J.*, 1920, **14**, 267—281).—The apparatus contains two improvements on the usual arrangements. The more important of these is the use of three separate gas burettes, the first being used exclusively for moving the air to and from the absorption pipettes, the second being of a size suitable for measuring the air before and after the absorption of carbon dioxide, and the third is for measuring the air after the absorption of oxygen. The water vapour necessary for saturating the sample of air, after it comes from the absorption pipettes, is supplied by the first burette. The other two burettes contain just enough water to ensure that the samples remain saturated.

The second improvement is that the mercury is raised and lowered in the burettes, not by raising and lowering a mercury reservoir, but by means of air pressure. This obviates the use of rubber connexions between the burettes and the reservoirs, and also considerably facilitates the analytical manipulations.

The apparatus is fully sketched in the original, and detailed instructions are given for conducting an analysis. W. G.

**Titration with the Hydrogen Electrode.** W. D. TREADWELL and L. WEISS (*Helv. Chim. Acta*, 1920, **3**, 433—446).—The authors describe a hydrogen electrode which, when in steady use, retains its activity for six weeks, and is then easily regenerated. The change in potential of the electrode during acidimetric titrations may be measured with sufficient accuracy by means of a millivoltmeter, and it may be used for the titration of both strong and weak acids. With the latter, the equilibrium constants may be calculated very simply from the fall in potential during the

titration. Strong acids in presence of weak acids may also be estimated.

T. H. P.

**Standardisation of Sodium Thiosulphate, Arsenious Acid, Potassium Bromate, Potassium Iodate, etc., Solutions, by means of Standard Sulphuric Acid Solution.** L. BERTIAUX (*Ann. Chim. anal.*, 1920, [ii], 2, 207—208).—The equivalent quantity of iodine liberated from a mixture of potassium iodate and potassium iodide by a definite volume of standard sulphuric acid solution is used for the standardisation of thiosulphate and arsenious acid solutions. Variations of the reaction are employed for the standardisation of the other solutions mentioned.

W. P. S.

**Indicators used for Estimating Free Acid in Pickling Solutions.** C. L. BOYLE (*J. Ind. Eng. Chem.*, 1920, 12, 571—572).—Sodium or potassium thiocyanate solution is recommended as the indicator, since the end-point shown by ordinary indicators is obscured by the large amount of ferrous sulphate present in the pickling solution.

W. P. S.

**The Incineration of Organic Substances Prior to Analysis for the Mineral Elements which they Contain. Application to the Analysis of Blood.** A. DESGREZ and J. MEUNIER (*Compt. rend.*, 1920, 171, 179—182).—For the incineration of organic substances for subsequent ash analysis, the authors recommend that the material should first be thoroughly dried, and then ignited and allowed to burn at as low a temperature as possible. In this way, a carbonised material is obtained which, when further incinerated, readily becomes incandescent and leaves a white ash. If excess of alkali salts is present, these should be extracted with water before the final incineration. This method has been applied to the ash analysis of blood, and the presence of copper, manganese, and lithium detected.

W. G.

**Volumetric Estimation of Sulphuric Ions.** JOSEPH ERLICH (*Ann. Chim. anal.*, 1920, [ii], 2, 214—215).—The solution, containing about 0.01 gram of sulphuric acid as alkali salt, is neutralised, boiled with the addition of barium carbonate, set aside for twelve hours, filtered, the precipitate washed, and the alkalinity of the filtrate titrated with *N*/10-acid. The alkalinity is equivalent to the sulphuric ions present originally.

W. P. S.

**Estimation of Nitrate Nitrogen in Nitrates and Fertilisers.** H. C. MOORE (*J. Ind. Eng. Chem.*, 1920, 12, 669—673).—From 0.8 to 1.7 gram of the sample, according to the quantity of nitrate present, is mixed with 35 c.c. of sulphuric acid containing 1 gram of salicylic acid, the mixture is shaken for fifteen minutes, 5 grams of sodium thiosulphate are added, and the mixture heated until frothing ceases. Five grams of potassium sulphate and 0.5 gram



of mercury are then added, and the heating is continued for ninety minutes after a clear solution has been obtained. Sodium sulphide is added in the subsequent distillation of the ammonia.

W. P. S.

**Preparation of Diphenylamine-sulphuric Acid.** FR. HAUN (*Zeitsch. Nahr. Genussm.*, 1920, **39**, 355—356).—The sulphuric acid used in preparing diphenylamine reagent for the detection of nitrates should be free from nitric acid, as shown by the brucine test. Sometimes the reagent made with sulphuric acid free from nitric acid becomes blue in colour after a short time; this is due to the presence of ferric salts in the sulphuric acid. Such acid may still be used if it is heated previously to boiling and then cooled; the ferric salts are reduced permanently by this treatment, and the acid does not give a blue coloration when mixed with diphenylamine. The course of the reduction may be followed by adding a trace of permanganate before heating the acid. The permanganate is also reduced, and the presence of the manganese tends to increase the sensitiveness of the reagent. W. P. S.

**Iodic Acid as a Characteristic Microchemical Reagent for Gaseous Ammonia.** GEORGES DENIGÈS (*Compt. rend.*, 1920, **171**, 177—179).—When one drop of a 10% aqueous solution of iodic acid is exposed to an atmosphere containing ammonia, it immediately becomes covered with a crystalline film. These crystals may readily be identified under the microscope as flattened, quadratic crystals of the normal iodate,  $\text{NH}_4\text{IO}_3$ . None of the volatile amines examined gave this reaction under these conditions. For the detection of traces of ammonium salts in a solution, the latter is first concentrated by evaporation, and then the ammonia is liberated by the action of magnesium oxide and tested as above.

W. G.

**The Technique of the Estimation of Phosphoric Acid as Barium Phosphomolybdate.** S. POSTERNAK (*Bull. Soc. chim.*, 1920, [iv], **27**, 564—568).—Very full details are given for preparing the solutions for, and conducting an estimation by, the method already described (this vol., ii, 505).

W. G.

**Estimation of Solvent Carbon Dioxide in Water.** H. NOLL (*Zeitsch. angew. Chem.*, 1920, **33**, i, 182—184).—It was shown by Tillmans and Heublein (A., 1913, ii, 51) that free carbon dioxide in soft water has a much greater solvent action on calcium carbonate than the same amount of carbon dioxide in hard water, since that portion required to keep calcium hydrogen carbonate, etc., in solution has no solvent action on calcium carbonate. Curves plotted by Tillmans and Heublein enable the amount of solvent carbon dioxide to be read directly when the amounts of free and combined carbon dioxide are known. In the case of waters containing iron hydrogen carbonate, the semi-combined and the combined

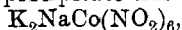
carbon dioxide in the iron compound are titrated simultaneously with the free carbon dioxide, and, as a correction, 1.1 mg. of carbon dioxide must be deducted for each mg. of ferric oxide present. For this reason, the filtrate from plants used for removing iron from water will often yield higher values for free carbon dioxide than the original water. The combined carbon dioxide in water may be estimated by titration with hydrochloric acid, with methyl-orange as indicator, and also by boiling the water with excess of acid and titrating the excess, with phenolphthalein as indicator. The carbon dioxide in combination with iron is estimated by the first method, but not by the second. The results for solvent carbon dioxide in waters free from iron are most trustworthy when, in addition to calcium hydrogen carbonate, the water also contains considerable quantities of the hydrogen carbonates of magnesium and sodium. The solvent action of free carbon dioxide is probably reduced to the greatest extent by iron hydrogen carbonate, and successively less by the hydrogen carbonates of calcium, magnesium, and sodium.

C. A. M.

**Hæmato-respiratory Functions. II. The Henderson-Morriss Method for Determining the Carbon Dioxide in Plasma and in Whole Blood.** HOWARD W. HAGGARD (*J. Biol. Chem.*, 1920, **42**, 237—244).—A careful study of the Henderson-Morriss method (A., 1917, ii, 506) of determining the carbon dioxide of plasma or whole blood, and a comparison with the method of Van Slyke and Cullen (A., 1917, i, 521), show that the various corrections almost exactly neutralise each other. At ordinary temperatures and barometric pressures, the reading on the gas burette for the carbon dioxide absorbed during the gas analysis (corrected only for the carbonate of the ammonia solution) may be taken as indicating directly, within the error of the method, the amount of carbon dioxide contained in the blood or plasma. With this method, the analysis of whole blood is as easy as that of plasma.

W. G.

**Estimation of Potassium and its Separation from Sodium by means of Sodium Cobaltinitrite.** P. WENGER and C. HÉMEN (*Ann. Chim. anal.*, 1920, [ii], **2**, 198—199).—The potassium sodium cobaltinitrite precipitate, obtained in the usual way, is dissolved in hydrochloric acid, and the cobalt then estimated electrolytically or gravimetrically. The precipitate has the composition



and the potassium may be calculated from the weight of cobalt found.

W. P. S.

**Titration of Ammonium Hydrogen Fluoride.** WALLACE S. CHASE (*J. Ind. Eng. Chem.*, 1920, **12**, 567—568).—Methyl-orange, litmus, lacmoid, methyl-red, and cochineal are untrustworthy as indicators in the presence of free hydrofluoric acid, and ammonia interferes with the sensitiveness of phenolphthalein. If,

however, the ammonium hydrogen fluoride solution is treated with an excess of calcium chloride, the hydrochloric acid liberated may be titrated, using methyl-orange as indicator. There is no need to remove the precipitated calcium fluoride by filtration.

W. P. S.

**Estimation of Calcium by Different Methods.** GEORGE E. ÉWE (*Chem. News*, 1920, 121, 53—56).—The following average results were obtained in the estimation of calcium in a sample of calcite by different methods: (1) precipitation as calcium oxalate and weighing as calcium carbonate, 99.57%; (2) precipitation as calcium carbonate and weighing as such, 100.07%; (3) liberation of carbon dioxide with hydrochloric acid and weighing the carbon dioxide in potassium hydroxide solution, 100.03%; (4) precipitation as calcium oxalate and weighing as calcium oxide, 99.86%; (5) precipitation as calcium sulphate and weighing as such, 99.68%; (6) precipitation as calcium oxalate and weighing as calcium sulphate, 100.39%; (7) precipitation as calcium oxalate and titration with potassium permanganate, 99.68%; (8) precipitation as oxalate from a slightly acid solution, 99.87%; (9) liberation of carbon dioxide and calculation of loss into  $\text{CaCO}_3$ , 99.80%; (10) residual titration method, 99.75%. The theoretical amount of calcium (as  $\text{CaCO}_3$ ) in the material was 99.959%. C. A. M.

**Acidity and Acidimetry of Soils. III. Comparison of Methods for Estimating Lime Requirements of Soils with Hydrogen Electrode. IV. Proposed Method for Estimation of Lime Requirements of Soils.** HENRY G. KNIGHT (*J. Ind. Eng. Chem.*, 1920, 12, 559—562).—The vacuum method (A., 1916, i, 459) appears to be the most trustworthy for estimating the lime requirement of soils, and the hydrogen electrode method (this vol., i, 587) yields results which agree with those given by the vacuum method, provided that the soil is shaken with lime for more than three hours before the hydrogen-ion concentration is determined. The Hopkins (A., 1916, i, 459) and hydrogen electrode methods are the best for measuring the reduction of acidity in limed soils. A method proposed for estimating the lime requirements of soils consists in boiling a mixture of 10 grams of the soil, 25 c.c. of normal potassium chloride or sodium chloride solution, and an excess of calcium carbonate for ten minutes, and measuring the volume of the carbon dioxide evolved. The results obtained agree with those found by the hydrogen electrode method. W. P. S.

**Rapid Identification of the Two Ionic Elements of Barium Sulphate.** G. DENIGÈS (*Bull. Soc. chim.*, 1920, [iv], 27, 560—564).—A more detailed account of work already published (compare this vol., ii, 398). W. G.

**Estimation of Lead in Chemicals in Acid Solution.** NORMAN EVERS (*Pharm. J.*, 1920, 105, 85—86).—In the colorimetric (sulphide) estimation of lead in acid solution, the test

solution and the comparison solution should have the same hydrogen-ion concentration, otherwise the colorations obtained are not comparable. The author recommends that the acidity should be neutralised before the sulphide is added, and that bromo-phenol-blue (tetrabromophenolsulphonphthalein) should be used as the indicator; this indicator is colourless at the neutral point. Iron does not interfere under these conditions, and the effect of copper may be prevented by the addition of cyanide. If both iron and copper are present, the copper should be separated by adding alum solution and ammonia, collecting the aluminium hydroxide (this precipitate also contains the lead), dissolving it in acid, and treating this solution as described, but without the addition of cyanide.

W. P. S.

**Estimation of Mercury in Organic Combination by means of Zinc Filings.** MAURICE FRANÇOIS (*Bull. Soc. chim.*, 1920, [iv], 27, 568).—A simplification of the method previously described (this vol., ii, 269), which avoids the necessity for heating. About half a gram of the dry, powdered organic matter is weighed into a tared, conical flask. To it is added 30 c.c. of ether, 10 c.c. of alcohol, 1 c.c. of concentrated hydrochloric acid, and, immediately, 1 gram of zinc turnings. The mixture is shaken once and left for half an hour. Another gram of zinc is added, the mixture shaken, and again left for half an hour, when a third gram of zinc is added, and the mixture left twenty-four hours. By this time all the mercury is deposited on the zinc, and the estimation is continued as described (*loc. cit.*).

W. G.

**Modification of Caron and Raquet's Reaction for Manganese.** G. DENIGÈS (*Ann. Chim. anal.*, 1920, [ii], 2, 215—216).—This reaction (A., 1919, ii, 351, 438) may be simplified as follows: 5 c.c. of the manganese solution and a few drops of sodium hydroxide solution are shaken thoroughly in a test-tube until a brown coloration is obtained; saturated oxalic acid solution is then added drop by drop. The brown coloration disappears and the characteristic red coloration develops.

W. P. S.

**The Use of Phenolphthalein and Diphenylamine in the Method with Persulphate for the Estimation of Manganese.** D. H. WESTER (*Rec. trav. chim.*, 1920, 39, 600—602. Compare this vol., ii, 451).—The author finds that the use of an alkaline solution of phenolphthalein as a comparison solution, and of diphenylamine for deepening the colour, in the estimation of manganese colorimetrically, as recommended by Tillmans and Mildner (A., 1915, ii, 583), does not give exact results.

W. G.

**Estimation of Manganese in Biological Material together with Data on the Manganese Content of Human Blood and Tissues.** CLARENCE K. REIMAN and ANNIE S. MINOT (*J. Biol. Chem.*, 1920, 42, 329—345).—For the preliminary preparation of

the tissue or blood, by means of which any manganese present is converted into the sulphate, the authors recommend either a modification of Bertrand's method (compare A., 1912, ii, 459, 662), the fusion with potassium acid sulphate being carried out at 500—600° in quartz vessels, or the digestion with sulphuric, nitric, and hydrochloric acids in pyrex Kjeldahl flasks. It is noted that quartz vessels are liable to contain manganese, and must be tested by a preliminary fusion. For the conversion of the manganese sulphate into permanganate, the authors further slightly modify Bertrand's modification (*loc. cit.*) of Marshall's method (compare *Chem. News*, 1901, 83, 76) with potassium persulphate.

A series of results is given for the manganese content of human blood, the values obtained varying from 0.004 to 0.02 mg. per 100 grams, most of the cases coming between the limits 0.01 and 0.02 mg. No abnormality in manganese content was shown by the few pathological cases examined, except, perhaps, in the case of syphilis of long duration, where the manganese is low.

The results for the manganese contents of human organs from fourteen autopsies are given, manganese being invariably present. The liver has the highest manganese content, 0.17 mg. per 100 grams of wet tissue on the average.

W. G.

### Estimation of Small Quantities of Iron as Thiocyanate.

RICHARD WILLSTÄTTER (*Ber.*, 1920, 53, [B], 1152—1154).—Small amounts of iron, such as are found in peroxylase preparations, can be estimated rapidly and accurately in the following manner. The solution under investigation (0.5—1 c.c.) is treated with concentrated hydrochloric acid (0.5 c.c.) and made up to 50 c.c. with freshly prepared ammonium thiocyanate solution (40%, or, with larger quantities of iron, 10%). The coloration is matched by the use of standard solutions of iron, which are similarly treated. Difficulties are caused by the presence of iron in the purest commercial ammonium thiocyanate and by the instability of ferric thiocyanate in solution; the latter effect is due to the gradual reduction of the ferric salt by the thiocyanate, but the process does not appear to be catalysed by the ferrous salt formed. The difficulty first named is overcome by boiling the ammonium thiocyanate solution for a short time, after which it remains colourless when cooled.

H. W.

**Use of Potassium Xanthate for the Detection and Separation of Cobalt in the Presence of Nickel.** LOUIS COMPIN (*Bull. Sci. Pharmacol.*, 1920; from *Ann. Chim. anal.*, 1920, [ii], 2, 218—220).—When a solution containing nickel and cobalt is acidified with hydrochloric acid and treated with a slight excess of potassium xanthate, the two metals are precipitated as xanthates. On the addition of ammonia, the nickel compound dissolves to give a blue solution, whilst the cobalt compound remains insoluble. When this method is used for the estimation of cobalt in nickel,

the ammoniacal solution of the cobalt compound should be acidified with hydrochloric acid, and the precipitation repeated in order to recover a trace of cobalt which dissolves in the ammonia.

W. P. S.

**Estimation of Zirconium and Titanium in Zirconium Ores.** G. E. F. LUNDELL and H. B. KNOWLES (*J. Amer. Chem. Soc.*, 1920, **42**, 1439—1448).—A method of estimating zirconium, titanium, and the total rare earths in zirconium ores, is described. The method is found to be applicable in the presence of any or all of the elements which have ever been found in zirconium ores.

Four grams of borax are fused and allowed to solidify in a platinum crucible, 0.3 gram of finely powdered ore (100 mesh) added, and the mixture heated over a Meker burner and stirred with a platinum rod for thirty minutes. The cooled mass is placed in hydrochloric acid (1:5) in a beaker and warmed on a steam-bath. The solution is transferred to a platinum dish, treated with sulphuric acid (1:20), and evaporated until fumes of acid are evolved. The concentrated liquid is cooled, diluted to 100 c.c., and the impure silica filtered off and washed, and the washings added to the filtrate. The filtrate is warmed overnight to precipitate small amounts of phosphorus as zirconium phosphate. The precipitate is filtered and washed with 5% ammonium nitrate, and the washings added to the filtrate. Ammonium chloride (5 grams) is added to the filtrate, followed by an excess of ammonia, and the solution boiled for a few minutes, filtered, and the precipitate washed with 2% ammonium nitrate, and the filtrate discarded. The precipitate is dissolved in hot 5% sulphuric acid and the paper thoroughly washed (solution A). The filter paper, together with the filter papers containing the silica and the zirconium phosphate, is ignited in the original crucible, the ash moistened and treated with 1 c.c. of sulphuric acid and 5 c.c. of hydrofluoric acid, and ignited until all the sulphuric acid is expelled. The residue is ignited with a small amount of sodium carbonate. The fused mass is digested with water and filtered. The residue is well washed with hot water, ignited, and fused with sodium hydrogen sulphate; the cooled fusion is dissolved in 5% sulphuric acid, and the solution added to the solution A. The foregoing treatment removes phosphoric acid and recovers any zirconium which was present in the silica. The solution containing the whole of the metals is neutralised until it contains about 1% (by volume) of free sulphuric acid, treated with hydrogen sulphide, and filtered if necessary. The filtrate is made up to 200 c.c., treated with tartaric acid in amount equal to five times the weight of the bases in solution, made ammoniacal, and saturated with hydrogen sulphide, and any sulphide filtered off. The acidity of the solution is brought to 10% of sulphuric acid in a volume of 400 c.c., the solution boiled to expel hydrogen sulphide, and cooled to 4—15°. An excess of a cold 6% aqueous solution of cupferron is added. An excess is indicated by a fine, white precipitate, which

redissolves, instead of a curdy one, which remains. After digesting for five minutes, the precipitate is filtered with gentle suction, washed with 10% (by volume) hydrochloric acid, and dried. The paper and precipitate are ignited in a weighed platinum crucible over a blowpipe flame, and weighed. The weight is that of the oxides of zirconium, titanium, and the rare earth metals. After weighing, the oxides are fused with potassium hydrogen sulphate, taken up with 10% (by volume) sulphuric acid, and diluted to exactly 100 c.c. This is divided into two 50 c.c. portions, and the titanium estimated in one and the rare earths in the second, and the zirconium obtained by difference. *Estimation of titanium.*—If the content of titanium is low, it is estimated by Weller's colorimetric method, whilst if it is high, it is reduced to the sesquioxide in a Jones' reductor containing ferric alum and phosphoric acid in the receiver, and then oxidised to the dioxide by titration with potassium permanganate. *Estimation of the rare earths.*—The hydroxides are precipitated with excess of potassium hydroxide, filtered, washed, and then washed into a platinum dish with 5% hydrofluoric acid. The solution is evaporated nearly to dryness and treated with 5 c.c. of 5% hydrofluoric acid. If no precipitate is present, the rare earths are absent; if present, it is filtered, washed with 5–10 c.c. of the same acid, transferred to a platinum dish, and ignited. Sulphuric acid is then added, and the whole evaporated to dryness, dissolved in dilute hydrochloric acid, and the rare earth hydroxides precipitated with ammonia, filtered, washed, redissolved in hydrochloric acid, and evaporated to dryness. The residue is treated with 5 c.c. of boiling 5% oxalic acid solution, and, after digesting for fifteen minutes, filtered, washed with 20 c.c. of 5% oxalic acid, ignited, and weighed. The accuracy of the method is shown by a series of concordant analyses of diorite to which weighed amounts of zirconium, titanium, thorium, cerium, and phosphate had been added. J. F. S.

**Estimation of Zirconium in Steel.** G. E. F. LUNDELL and H. B. KNOWLES (*J. Ind. Eng. Chem.*, 1920, **12**, 562–567).—A critical review of methods published previously. The authors also give a method for the estimation of silicon, aluminium, titanium, and zirconium in steels which may contain other elements, such as tungsten, chromium, vanadium, phosphorus, molybdenum, copper, nickel, cobalt, uranium, and cerium. The steel is dissolved in hydrochloric acid with the addition of nitric acid, silica is separated, the greater part of the iron removed by extraction with ether, the hydrochloric acid solution then treated with excess of sodium hydroxide, and the precipitate collected. This precipitate is dissolved in hydrochloric acid, the solution nearly neutralised, tartaric acid is added, the mixture treated with hydrogen sulphide, then rendered ammoniacal, and filtered. After the filtrate has been acidified with sulphuric acid and boiled to expel hydrogen sulphide, the zirconium and titanium are precipitated together by "cupferron"; the titanium is estimated subsequently, either

colorimetrically or volumetrically, in the mixed oxides. [See, further, *J. Soc. Chem. Ind.*, 1920, September.] W. P. S.

**Immediate Analysis by Fractional Distillation, Method of Maxima and Minima.** CHARLES MOUREU, CHARLES DUFRAISSE, and PAUL ROBIN (*Bull. Soc. chim.*, 1920, [iv], 27, 523—527).—The method described, which is applicable to the separation of mixtures of substances with boiling points close together, consists of successive fractional distillations, the division into fractions being controlled, not by the boiling points, but by maximum or minimum values of physical properties, such as density, refractive index, viscosity, etc. The rectification is continued, similar fractions being united for further fractionation, until a fraction is obtained which, when subdivided by slow distillation, gives fractions all of which possess identical boiling points and physical properties.

A simple vaselin manometer is described by means of which very slight variations in pressure during distillation may be noted, and it allows of a distillation being interrupted and then very readily resumed at the same reduced pressure. W. G.

**Critical Study of Methods for the Detection of Methyl Alcohol.** ALEXANDER O. GETTLER (*J. Biol. Chem.*, 1920, 42, 311—328).—Fifty-eight tests for the detection of methyl alcohol were critically studied to ascertain their trustworthiness, specificity, and sensitiveness, and the influence of foreign substances on them. They may be divided into two groups: (1) in which the methyl alcohol is oxidised to formaldehyde, which is then detected; (2) in which direct tests for methyl alcohol itself are applied. As oxidising agents for conversion of the methyl alcohol into formaldehyde, the author prefers alkaline permanganate or potassium dichromate and sulphuric acid. The colorimetric tests for the detection of formaldehyde which he considers most trustworthy are: with (1) phenylhydrazine+ferric chloride+hydrochloric acid (Meth, A., 1906, ii, 588); (2) phenylhydrazine+sodium nitroprusside+sodium hydroxide (Meth, *loc. cit.*); (3) apomorphine sulphate (Wolff, A., 1919, ii, 482); (4) peptone+ferric chloride+hydrochloric acid (Salkowski, A., 1919, ii, 249); (5) reduced magenta+sulphuric acid (Denigès, A., 1910, ii, 357, 461). These colour tests are extremely sensitive, 1 part in 200,000 being easily detected. Two confirmatory tests in which crystalline products are obtained are: (1) with  $\beta$ -naphthol+hydrochloric acid (Mulliken, "A method for the identification of pure organic compounds," 1911); (2) with concentrated ammonia, giving hexamethylenetetramine, which gives characteristic crystals with mercuric chloride (Romijn, A., 1896, ii, 280). These two tests require the presence of 5% of methyl alcohol.

All the methods, which are applied directly for methyl alcohol, require a large amount of methyl alcohol. Of the twelve examined, the method of Leach and Lythgoe (A., 1905, ii, 655), in



which the relationship between specific gravity and refractive index is determined, is the most outstanding. As a colorimetric test, that described by Vivario (A., 1914, ii, 780), in which the alcohol is converted into potassium cyanide, is very good.

Details of the typical procedures for the detection of methyl alcohol in liquors and in tissues are given, and there is a full bibliography. W. G.

**Diazometric Estimation of Phenol and of certain of its Homologues.** ROBERT M. CHAPIN (*J. Ind. Eng. Chem.*, 1920, 12, 568—570).—The method depends on the coupling of phenols with diazonium salts to form insoluble hydroxyazo-compounds. The reagent is prepared by mixing equal volumes of *N*/10-*p*-nitro-aniline solution and 1% sodium nitrite solution, and is standardised against  $\beta$ -naphthol. The phenol solution to be titrated is treated with 10% sodium acetate solution and basic lead acetate solution, and the reagent is added with constant stirring. Small, filtered portions of the mixture are tested from time to time with a drop of the reagent or a drop of phenol solution in order to ascertain the progress of the titration. [See, further, *J. Soc. Chem. Ind.*, 1920, September.] W. P. S.

**Analysis of Phenolsulphonic Acids.** LOUIS DESVERGNES (*Ann. Chim. anal.*, 1920, [ii], 2, 211—214).—About 5 grams of the sample are dissolved in water and diluted to 200 c.c. Ten c.c. of the solution are boiled for fifteen minutes with hydrochloric acid and bromine, diluted to 200 c.c., cooled, filtered, and the sulphuric acid is estimated in the filtrate as barium sulphate; this gives the total sulphuric acid ( $H_2SO_4$ ) present. Ten c.c. of the solution are then titrated with *N*/2-sodium hydroxide solution, using methyl-orange as indicator; the combined sulphuric acid is calculated from the formula  $(T-S)/2$ , where *T* is the total sulphuric acid and *S* the sum of the total sulphuric acid and one-half of the combined sulphuric acid. The phenol is estimated by treating 10 c.c. of the solution with 100 c.c. of water and 50 c.c. of hydrochloric acid, adding a definite quantity of standardised potassium bromide-bromate solution, heating the mixture at 50° for thirty minutes in a closed vessel, and then titrating (iodometrically) the excess of bromine. Calculation gives the amount of free sulphuric acid present, and the proportion of phenol to combined sulphuric acid indicates the amounts of mono- and di-sulphonic acids in the sample. W. P. S.

**Use of Potassium Ferrocyanide in the Analysis of Sugars by Alkaline Copper Solutions.** E. CORDONNIER (*Bull. Sci. pharmacol.*, 1920, 27, 137—138).—The use of potassium ferrocyanide, in the amounts indicated by its advocates, is capable of causing a complete reduction of Fehling's solution if the boiling is sufficiently prolonged. The method of Causse-Bonnans leads to

very serious errors if the conditions of heating are not accurately controlled.

CHEMICAL ABSTRACTS.

### Blood Sugar Concentration and Blood Sugar Methods.

H. F. HÖST and ROLF HATLEHOL (*J. Biol. Chem.*, 1920, **42**, 347—358).—Bang and Hatlehol's method (compare A., 1918, ii, 279), and Hagedorn and Jensen's method (compare *Ugesk. Læger*, 1918, **80**, 1217), give in normal individuals and in diabetics values for the blood sugar concentration which agree approximately. The method of Folin and Wu (A., 1919, ii, 308), and particularly the modification by Myers and Bailey (A., 1916, i, 300) of Benedict's method, may, in the case of diabetics with hyperglycæmia, give results which are too high.

W. G.

### Method for the Estimation of Acetic Acid in Acetates.

OSCAR A. PICKETT (*J. Ind. Eng. Chem.*, 1920, **12**, 570—571).—Xylene is used in place of water as a carrier for the acetic acid in the distillation of the acetate with phosphoric acid. About 350 c.c. of xylene are used for 2.5 grams of the acetate, and the distillation is continued until only a thin film of xylene remains on the surface of the phosphoric acid solution in the distillation flask.

W. P. S.

**Degree of Alkalinity Necessary for the Phloroglucinol Test for Formaldehyde.** PAUL J. HANZLIK (*J. Biol. Chem.*, 1920, **42**, 411—413).—The degree of alkalinity necessary for a minimum positive reaction in the phloroglucinol test for formaldehyde is  $P_H = 12.13$ , or the equivalent of the alkalinity of 0.01*N*-sodium hydroxide. For an optimum reaction, the alkalinity should be  $P_H = 13.0$ , or 0.1*N*.

W. G.

### Estimation of Acetaldehyde in Paracetaldehyde.

W. STÜWE (*Apoth. Zeit.*, 1920, **35**, 153—154; from *Chem. Zentr.*, 1920, iv, 155).—Paracetaldehyde (5 c.c.) is brought into a 100 c.c. flask and frequently shaken during a quarter of an hour with *N*/10-mercuric chloride solution (10 c.c.), potassium iodide free from iodate (2 grams), sodium hydroxide solution (15%, 20 grams), and water (50 grams). The mixture is diluted to 100 c.c. and filtered. Fifty c.c. of the filtrate are treated with gum arabic (0.5 gram), sodium hydroxide solution (5 c.c.), and formaldehyde (3 c.c.); after two minutes, the solution is acidified with dilute acetic acid (15 c.c.), and subsequently cooled. The precipitated mercury is dissolved by addition of a measured volume of *N*/10-iodine solution, and excess of the latter is titrated.

H. W.

**Rapid Volumetric Methods for the Estimation of Aminoacids, Organic Acids, and Organic Bases.** FREDERICK WILLIAM FOREMAN (*Biochem. J.*, 1920, **14**, 451—473).—Ammonia, primary, secondary, and tertiary amines, and basic methylene derivatives of secondary amines do not form ionisable compounds with phenolphthalein in aqueous-alcoholic solutions providing the concentration of alcohol is above 80%. In such solutions, therefore,

the acid radicles of the salts of these bases can be titrated accurately with *N*/10-potassium hydroxide, using phenolphthalein as indicator. Similarly, when aqueous-alcoholic solutions of certain amino-acids containing about 85% of alcohol are titrated with *N*/10-alcoholic potassium hydroxide, the amino- or imino-groups, liberated from their "internal salt" combinations, show no basicity to phenolphthalein, and the carboxyl groups are accurately estimated. Certain amino-acids, however, more particularly bibasic amino-acids and proline, give low results when titrated in alcohol under these conditions, possibly owing to loose combination of alcohol with a carboxyl group, or loose condensation, but a subsequent addition of formaldehyde or acetone results in a disturbance of the equilibrium, and then the carboxyl groups can be titrated quantitatively.

The guanidine nucleus of arginine behaves differently from other nitrogenous bases or basic groups in that it acts as a univalent base in both alcohol and water. Thus it is neutral to phenolphthalein in 85% alcohol solution, the carboxyl group and the guanidine nucleus exactly neutralising each other.

The complete estimation is carried out as follows: (1) Five c.c. of the aqueous solution are titrated with *N*/10-aqueous sodium hydroxide. (2) Ten volumes of 97% alcohol are added to 5 c.c. of the aqueous solution, and the mixture is titrated with *N*/10-alcoholic potassium hydroxide. (3) To the liquid from titration (2), 12.5 c.c. of neutral 13% aqueous formaldehyde solution are added for every 50 c.c. of alcohol present, and the titration continued to the same end-point. Titration (1) gives useful information when dibasic amino-acids, arginine, and salts of amino-acids are present. Titration (2) gives the correct estimation of a number of amino-acids. In titration (3), the carboxyl groups of all the amino-acids in an amino-acid mixture, except that of arginine, are estimated.

This new volumetric process forms a rapid and accurate method for use in the investigation of many important biochemical problems. For the estimation of volatile bases and amino-acids in "alcoholic extracts" (compare Foreman and Graham-Smith, *J. Hygiene*, 1917, **16**, 144), to an aliquot part of the extract the amount of alcoholic alkali necessary for neutralisation, as determined by titration (3), is added, and the mixture is distilled with steam free from carbon dioxide for about five minutes, the distillate being collected in standard acid. The excess of acid is titrated, using alizarin as indicator, and thus a measure of the volatile bases is obtained. The residual liquid in the distillation flask is free from alcohol, and, owing to the hydrolysis of the alkali salts of the amino-acids, is alkaline. It is titrated with *N*/10-acid, and thus a value is obtained for the amino-acids present in the original "alcoholic extract."

W. G.

#### Micro-estimation of Urea in Blood by means of Urease.

R. BAHLMANN (*Ned. Tydsch. Geneesk.*, 1920, **64**, [i], 473—478; from *Chem. Zentr.*, 1920, iv, 3—4).—The method of Cohen,

Fervaert, and Van Lier is modified in such a manner that the estimation can be made with 0.4 c.c. of blood. The ammonia, obtained by the action of the urease of the soja bean on the urea of the blood in faintly acid solution, is, after addition of alkali, drawn by a stream of air into very dilute hydrochloric acid, and excess of the latter is estimated iodometrically according to Bang's method. A blank experiment is performed with an equal quantity of blood without addition of urease. The amount of urea is calculated from the difference in the titrations in the two experiments. H. W.

**Estimation of Hydrocyanic Acid in Beans.** A. CZAPSKI (*Zeitsch. anal. Chem.*, 1920, **59**, 80).—Paraffin wax should not be used to prevent frothing of the contents of the distillation flask during the distillation of hydrocyanic acid from cyanogenetic beans; the wax inhibits partly the distillation of the acid, and less than one half of the amount of the latter actually present is found in the distillate. W. P. S.

**Direct Estimation of Mercury Fulminate in the Mixtures for Detonators.** M. D. MARQUEYROL (*Bull. Soc. chim.*, 1920, [iv], **27**, 448).—The mixture is extracted with a 5% solution of potassium cyanide, and the mercury is estimated by electrolysis in the extract. W. G.

**A Pyrrole Reaction.** E. SALKOWSKI (*Biochem. Zeitsch.*, 1920, **103**, 185—188).—The action of pyrrole on *p*-dimethylamino-benzaldehyde resembles that of indole, only it is less sensitive and is to a greater extent influenced by the addition of nitrite and fuming hydrochloric acid. The author points out the necessity of taking this fact into consideration when carrying out Ehrlich's reaction. S. S. Z.

**Combination of Fractionation with Spectrophotometry in Proximate Organic Analysis.** W. E. MATHEWSON (*J. Amer. Chem. Soc.*, 1920, **42**, 1277—1279).—The spectrophotometric method of estimating dyes may be applied to colourless organic compounds by first converting these into coloured compounds, which are separated from the excess of reagents or other coloured substances present by extraction with suitable solvents. Procedures are described for the estimation of sulphanilic acid, acetone, and  $\beta$ -naphthol, depending on their condensation, respectively, with picryl chloride, 2:4-dinitrophenylhydrazine, and diazotised sulphanilic acid. J. K.

**Justification of the Sublimate-Ammonia Process for the Estimation of Stercobilin.** R. GOUFFON (*Compt. rend. Soc. Biol.*, 1920, **83**, 344—346; from *Chem. Zentr.*, 1920, ii, 755).—A reply to Borrien's objections (this vol., ii, 520). E. H. R.

**The Extraction of Stercobilin.** M. BRULÉ and H. GARBAN (*Compt. rend. Soc. Biol.*, 1920, **83**, 342—344; from *Chem. Zentr.*, 1920, ii, 754—755).—The extraction of stercobilin from excrement by solvents, such as amyl alcohol, chloroform, a mixture of chloroform and thymol, or 95% alcohol, is not complete. The extraction is better from acidified solutions, but under these conditions a change of the colouring matter appears to be brought about through oxidation. E. H. R.

**Analysis of the Colouring Substances in Urine. I. The Division of Urine into Three Main Fractions as a Basis for the Analysis of its Colouring Substances.** M. WEISS (*Biochem. Zeitsch.*, 1920, **102**, 228—246).—The urine is divided into three fractions. Fraction I consists of the red colouring substances—the urobilin fraction. Fraction II contains the yellow colouring substances—the urochrome fraction. Fraction III is composed of the colourless proteic acids—the histidine fraction. Fraction I, which is obtained by precipitating the urine with neutral lead acetate, and does not contain the urochrome, is responsible for about three-quarters of the coloration of the urine. Fraction II is precipitated from the filtrate of fraction I with 10% alkali hydroxide. Besides urochrome, this fraction contains urochromogen, which differs from urochrome by the fact that it gives the permanganate and diazo-reactions, reduces silver salts, and darkens more intensely on keeping, when a melanin group is eliminated, which the author considers to be a phenol derivative. The presence of urochromogen can be detected better in fraction II than in the original urine. The colourless fraction contains proteic acids. A tryptophan derivative is also present in the urine, which cannot always be identified with the chromogen of urorosein. S. S. Z.

**Chemistry of the Proteins.** E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1920, **102**, 89—98).—In order to obtain proteins free from adhering impurities, such as the products of protein degradation, fats, lipoids, etc., the clear extract from the tissues is precipitated with five to six volumes of 90% alcohol and heated on a boiling-water bath. It is then filtered or centrifuged, and the residue treated with boiling absolute alcohol, and again with boiling ether. The protein powder thus obtained is further extracted with boiling water to remove the albumoses, peptones, and salts. The authors also describe a method for the detection and estimation of the higher polypeptides in the protein solution. The protein and the higher polypeptides are precipitated with boiling 90% alcohol. The precipitated fraction is then extracted with boiling water, and the nitrogen is estimated in the aqueous extract. Using this method, it is found that all colloidal protein solutions contain appreciable quantities of albumoses. One hundred c.c. of human serum contain a quantity of albumoses and peptones equivalent to 0.4 gram of Witte's peptone. S. S. Z.

**Rapid Estimation of Albumin in the Urine.** L. DUPUY (*Presse medicale*, 1920, **28**, 104).—The turbidity of a standard solution of albumin is compared with that of the urine under examination after each has been treated with Eschlach's citric-picric acid reagent.

CHEMICAL ABSTRACTS.

**The Separation of Serum Proteins.** M. PIETTRE and A. VILA (*Compt. rend.*, 1920, **170**, 1466—1468).—The serum is first neutralised by addition of *N*-hydrochloric acid. To it is added two and a-half times its volume of acetone. The precipitate is collected on a Buchner funnel, mixed with one volume of acetone, dried by suction, and washed with ether. The cake of proteins, without being broken up too much, is transferred to a dish, covered with water (70 c.c. for each 100 c.c. of serum originally taken), and left in contact with it for several hours. The water is then carefully decanted, and this process is repeated two or three times. Finally, the material is powdered and washed two or three times by centrifuging with water saturated with carbon dioxide. By this means, the insoluble proteins are obtained free from albumin. The washing waters are united, saturated with carbon dioxide, and filtered, and from the filtrate the albumin is precipitated by the addition of an equal volume of acetone.

In the aqueous-acetone liquors, the fats, lipoids, sugars, etc., can be estimated separately by the usual processes. W. G.

**New and Improved Method for the Recognition of Human Blood.** ANGELO DE DOMINICIS (*Boll. Chim. farm.*, 1920, **59**, 241—244).—A simple method for detecting human blood on a knife-blade or other non-absorbent surface consists in pouring on to the spot a very dense solution of celluloid in amyl acetate, allowing the solvent to evaporate, removing the dry pellicle by means of needles, and examining under the microscope the superficial layer of blood on the pellicle. If the latter cannot be removed from the blood-stained surface, it may be first thickened by a second application of the celluloid solution. T. H. P.

**"Thiocol."** C. A. GRAU (*Bull. Sci. pharmacol.*, 1920, **27**, 17—22).—A diagram of the crystals formed by the reaction of thiocol with mercurous nitrate is given, together with the directions for making this microchemical test. As with guaiacol, so with thiocol, it is possible to test various plants for oxydases in the presence of hydrogen peroxide. The roots of artichoke, dahlia, chard, and lucerne are suitable materials responding positively to the test. Thiocol can also be used to demonstrate the presence of oxydase in the blood, and as a measure of renal insufficiency. Its use in the latter connexion depends on its detection in the urine by the rose colour developed when a few drops of the urine are placed on artichoke root, together with hydrogen peroxide. Its use is apparently incompatible with the presence of resorcinol,  $\alpha$ -naphthol, and sodium salicylate.

CHEMICAL ABSTRACTS.

## General and Physical Chemistry.

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**Extension of the Balmer Series of Hydrogen and Spectroscopic Phenomena of Very Long Vacuum Tubes.** R. W. Wood (*Proc. Roy. Soc.*, 1920, [A], **97**, 455—470).—The author describes a type of vacuum tube in which it is possible to separate the secondary spectrum of hydrogen from the Balmer series. The tube is 2 m. long and has a 7 mm. bore, and is bent so that the central 40 cm. constitutes an "end on" tube, the electrodes of which are 80 cm. away from the tube. The electrodes are of aluminium; one end of the tube is in permanent connexion with a Gaede pump and the other is connected by a fine capillary tube with a hydrogen generator, either an electrolytic apparatus or a bulb containing palladium and hydrogen. The tube is operated at 25,000 volts and 0·2 ampere. When the pressure is such that there is a Crookes dark space of 4—5 cm., the ends of the tube show a bluish-white light, whilst the central portion shows a fiery purple colour, which exhibits the Balmer spectrum with a secondary spectrum of 1/40th the intensity of that in the side-tubes. It is possible by finer adjustment that the secondary spectrum may vanish entirely. The failure to observe more than twelve members out of the thirty-two emitted by solar hydrogen in the Balmer series is attributed to the numerous lines in the secondary spectrum, which are relatively brighter than the Balmer lines. On photographing the spectrum of the central portion of the tube the author has been able to observe all the Balmer lines up to the 20th. In the region of the 6th to the 14th line each line is practically twice as bright as its succeeding neighbour. This means, if this rate of change is continued, that the 20th line has an intensity of about 1/600,000 that of the  $H_\alpha$ -line. A number of other very interesting properties of the long tube are described. The following wavelengths have been measured: 12th line, 3722·12; 13th, 3712·22; 14th, 3703·92; 15th, 3697·35; 16th, 3691·72; 17th, 3686·99; 18th, 3682·96; 19th, 3679·46; 20th, 3676·44, all with reference to Rowland's iron standards. The influence of water vapour on the appearance of the secondary spectrum is described. J. F. S.

**Origin of "Cyanogen" Bands.** S. BARRATT (*Proc. Roy. Soc.*, 1920, [A], **98**, 40—49).—Observations have been made of the spectra of the flames of a number of gases containing carbon, hydrogen, nitrogen, and oxygen. The cyanogen bands are strongly developed in the coal gas-nitrous oxide flame. Evidence is obtained which shows that they are entirely absent from the hydrogen-nitrous oxide flame, if all traces of carbon are excluded, and it appears that carbon is essential to their production. The appearance of the cyanogen bands is, under appropriate conditions, a more delicate test for carbon than that of any other of the bands

associated with this element. On the other hand, this spectrum is not necessarily developed when both carbon and nitrogen are present. The conclusion of Grotrian and Runge, that the cyanogen spectrum is to be attributed to nitrogen, is shown to rest on assumptions which are not confirmed by the present work. The cyanogen spectrum provides a very delicate test for the presence of compounds of nitrogen admitted in the form of a gas to hydrocarbon flames burning in air, since elementary nitrogen does not appear, in ordinary circumstances, to be effective in producing cyanogen bands in such flames. The intensity of the cyanogen bands, when carbon compounds are admitted to the hydrogen-nitrous oxide flame, bears no simple relation to the amount of carbon thus added.

J. F. S.

**Character of the Light Radiations Emitted by the Vapours of Magnesium, Copper, and Manganese under the Selective Actions of Thermochemical and Thermoelectrical Excitations.** G. A. HEMSALECH (*Phil. Mag.*, 1920, vi, 40, 296—315).—With an electrically heated plate of graphite, which is not covered with a layer of carborundum, the red fringe (this vol., ii, 1, 2, and 170) appears on both sides. The upper fringe often extends to a greater distance from the plate than the lower one, probably on account of convection of vapours expelled from the under surface. The border of the upper fringe is sharply defined and its spectrum emission stops abruptly, in marked contrast to that of the luminous vapour. In the absence of sufficient quantities of ionised vapours, strong magnetic fields (1500—2000 C.G.S.) must be applied to displace the red fringe emission appreciably, hence the conclusion previously advanced, that the sharp outline is caused by the magnetic effect of the heating current, is untenable. No satisfactory alternative explanation is offered, but it is pointed out that most luminous phenomena which owe their origin to the flow of an electric current at atmospheric pressure present a sharp outline.

The vapours which fill the protected space are in great part derived from substances on the plate, and the formation of striæ at the boundary surface is interpreted as due to motion of the vapours round the plate in a helical path. The downward drift of luminous vapour in the protected space may be due to gravity or radiation pressure, or their combined action.

An investigation of the spectrum lines emitted by the vapours of magnesium, copper, and manganese showed that the line emissions due to thermoelectrical and chemical excitation are of the same type. The characteristic flame lines of magnesium, copper, and manganese, which in the air-coal gas flame are emitted by the mantle above the cone, all appear as long lines in the single plate furnace. This confirms their status as temperature lines.

J. R. P.

**The Fine Structure of the Near Infra-red Absorption Bands of Hydrogen Chloride, Bromide, and Fluoride.** H. M. RANDALL and E. S. IMES (*Physical Rev.*, 1920, 15, 152—155).—By



focussing on the slit of an infra-red grating spectrometer the spectrum produced by a prism spectrometer, using a salt prism of small refracting angle, the spectral region to be analysed is too short for the overlapping of spectra. It is possible to employ the full resolving power of a series of graded gratings with the result that in several instances the absorption curves show apparently complete resolution. The position of the narrow absorption bands can be determined with an accuracy of a few Å. In the case of the hydrogen chloride band at  $3.46\ \mu$ , each member of the broad doublet was resolved into twelve narrow bands. From the data obtained, the moment of inertia of the molecules of hydrogen chloride, hydrogen bromide, and hydrogen fluoride is calculated as well as the distance between the atoms in the molecule.

## CHEMICAL ABSTRACTS.

**The Object and Possibility of an Analysis of Absorption Spectra.** I. LIFSCHITZ (*Zeitsch. physikal. Chem.*, 1920, **95**, 1—14, 126. Compare this vol, ii, 208).—A theoretical paper, in which the object of absorption spectrum determination and the possibility of arranging absorption bands in some such series as are found for emission spectra are discussed. The reason for the latter is to remove absorption spectra from a purely empirical study and to find some connexion between the absorption bands and their arrangement and the chromophoric groups of the various substances. The term chromophore is redefined as follows. Chromophores are single atoms or groups of atoms which carry electrons capable of oscillation with frequencies between  $0.3$  and  $1.7 \times 10^{14}$ . J. F. S.

**Optical Effects Occasioned by Salt Formation with Organic Acids. I. Phenols and Enols.** H. LEY (*Zeitsch. physikal. Chem.*, 1920, **94**, 405—442).—The absorption spectra of a number of phenols, phenolic substances, alcohols, and their sodium derivatives have been measured in alcoholic solution by the Hartley method, using an iron arc as the source of light. The following combinations in various concentrations have been measured and recorded: phenol, and sodium phenoxide in ethyl alcohol and in water; *p*-xylenol, *m*-4-xylenol, thymol, *p*-chlorophenol, *p*-bromophenol, ethyl 2-naphthol-3-carboxylate, *o*-, *m*- and *p*-hydroxycinnamic acids and their ethyl esters, melilotic acid and its ethyl ester, *p*-methoxystilbene, *p*-hydroxystilbene, 2-hydroxydiphenyl, benzoyl-acetic ester,  $\beta$ -ethoxycinnamic acid and its ethyl ester, and the sodium derivatives of all the compounds in ethyl-alcoholic solution. Absorption curves have been drawn in all cases, and the changes in the absorption spectra brought about by the salt formation pointed out and considered in the light of the present results and other previously published work. J. F. S.

**Table for the Identification of Dyes by means of the Spectroscope.** JAMES MOIR (*J. S. African Assoc. Anal. Chem.*, 1920, **3**, 9—13).—The position of the centre of the absorption band of a large number of dyes is given, ranging from that of Aurantia at  $\lambda 425$  to that of tetramethylthionine at  $\lambda 668$ . W. P. S.

**Colour and Chemical Constitution. IV. The Remaining Phthaleins.** JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1919, 7, 183—188. Compare A., 1917, ii, 349, 557).—Further wave-length measurements of absorption bands are communicated of a number of derivatives, several new, of *pp'*- and of *op'*-phenolphthaleins, and of 4'-hydroxydiphenylphthalide. Quantitative conclusions are derived as to the percentage increase in wave-length of the absorption band of phenolphthalein due to the introduction of various substituents. In agreement with the view previously put forward as to the existence of secondary bands of the phthaleins with a wave-length two-thirds that of the visible band, phenolphthalein and thymolphthalein in alkaline solutions exhibit bands of which the edges are at  $\lambda$  380 and  $\lambda$  420 respectively. The centre of the band for *p*-cresolthymolphthalein in alkaline solution is at  $\lambda$  595, whilst the value calculated from those for phenol-*p*-cresol- and phenolthymolphthaleins is  $\lambda$  597.

By condensation of 5-bromoguaiacol with hydroxybenzoylbenzoic acid, the bromine atom is eliminated and phenolguaiacolphthalein is produced. In this compound, therefore, and presumably also in guaiacolphthalein, it is the methoxy-group which occupies the para-position to the central carbon atom (compare Hindmarsh, Knight and Robinson, T., 1917, 111, 941), and in dibromoguaiacolphthalein each bromine atom is in the ortho-position to the central carbon atom and also to one hydroxyl group in each nucleus. Quinonoid formulæ are suggested for the salts of quinolphthalein.

J. K.

**Colour and Chemical Constitution. V. The Yellowness of certain Phthaleins when Acid. VI. The Ultra-violet Spectra of the Phthaleins.** JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1919, 8, 41—44. Compare preceding abstract).—The absorption spectra of phenolsulphonophthalein, of benaurin-*p*-sulphonic acid, and of phenolphthalein monomethyl ether (Green and King, A., 1907, i, 933) only differ from that of benaurin in that the absorption band is moved slightly towards the red owing to the loading of the molecule with the sulphonic and carbomethoxy-groups respectively. Further, since all three compounds are yellow in slightly acid solution whilst phenolphthalein is colourless under these conditions, it is concluded that phenolsulphonophthalein is not a phthalein but benaurin-*o*-sulphonic acid.

Consideration of wave-length measurements by Howe and Gibson (*Physical Rev.*, 1917, 767) of the ultra-violet absorption bands from alkaline solutions of phenolphthalein and its derivatives leads to a modification of the earlier formula (A., 1917, ii, 350) to  $y = x - 7$ , indicating that in all phthaleins change of the grouping  $\text{:C} \begin{smallmatrix} \text{O} \\ \diagup \text{O} \end{smallmatrix}$  to  $\text{:C} \begin{smallmatrix} \text{OH} \\ \diagup \text{SO}_4\text{H} \end{smallmatrix}$  is accompanied by a diminution in frequency of 7 units.

J. K.

**Colour and Chemical Constitution. VII. Spectra of Solid Compounds of Cobalt, Nickel, Manganese, and Uranium.** JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1919, 8, 45—49. Compare preceding abstracts).—Evidence is adduced to show that the effect on the absorption spectrum of loading the molecule either internally by substitution or by combination with a non-ionising solvent noted in the case of certain organic compounds may also be observed among cobalt, nickel, and uranyl salts and among permanganates. It is noted that the wave-lengths of homologous lines of cobalt compounds, of uranyl compounds, and of the phthaleins are respectively proportional to the eighth, sixth, and fourth roots of the molecular weights of the compounds compared. J. K.

**Colour and Chemical Constitution. IX. An Empirical Law of Change of Colour.** JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1920, 8, 225—228. Compare preceding abstracts).—An examination of the absorption spectra of the haloid derivatives of phenolphthalein and fluorescein has shown that the effect of the substituents on the position of the bands is given by the relation  $\frac{n}{n_0} = 1 - \frac{m}{100} (1.15 + 0.0037N)$ , in which  $n$  = the frequency for the halogen derivative,  $n_0$  for that of the parent substance (18.05 for phenolphthalein and 20.27 for fluorescein),  $m$  = the number of substituent halogen atoms, and  $N$  = the atomic number of the halogen. The relationship also appears to hold approximately for alkyl derivatives. The view previously advanced that molecular volume is the main factor in colour change is abandoned in view of the fact that the introduction of methyl, isopropyl, chlorine, bromine, and iodine into the molecule produces about the same effect in each case. J. K.

**Colour and Chemical Constitution. VIII. Fluorescence and its Laws.** JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1919, 8, 51—53. Compare preceding abstract).—The emission spectra of the green fluorescences exhibited by uranyl compounds in the solid condition or in non-aqueous solution have been examined. The bands are equally spaced and probably always five in number, but usually some are too faint to be observed. It is found that for all of them  $\frac{A_n}{A_l} = \left(\frac{F_n}{F_l}\right)^{\frac{1}{2}}$ , in which  $A_n$  and  $F_n$  are corresponding wave-lengths in the absorption and fluorescent spectra, and  $A_l$  and  $F_l$  are the respective wave-lengths of the lowest bands in each. The relation also appears to hold for some organic compounds, which give much the same value, 1.15, for the ratio  $\frac{A_n}{A_l}$ . J. K.

**Scattering of Light by Dust-free Liquids.** W. H. MARTIN (*J. Physical Chem.*, 1920, 24, 478—492).—Dust-free liquids were prepared (i) by evaporation and condensation in an enclosed

exhausted apparatus, (ii) by precipitating gelatinous hydroxides of aluminium, cadmium, and zinc from dilute solutions of the sulphates, and (iii) by cataphoresis of water. The dust-free liquids were all found to scatter light, that of short wave-length being scattered to a much greater extent than that of long wave-length. A relationship,  $(\mu - 1)^2/n$ , formulated by Rayleigh and verified in the case of gases by Strutt, connecting the refractive index of the medium and its light-scattering power, showed some agreement in the case of the liquids investigated. The scattered light is very largely plane polarised in the case of liquids which scatter very little light, and the polarisation in different liquids decreases as the relative intensity of the scattered light increases. The polarisation is much less complete for liquids than for gases. Evidence is given to show that the phenomena observed are due to scattering and not to fluorescence. The following intensities of the scattered light are given in terms of that of toluene=1: water, 0.060; sulphur dioxide, 0.400; methyl alcohol, 0.160; ethyl alcohol, 0.180; ethyl ether, 0.236; ethyl acetate, 0.210; isobutyl chloride, 0.375; heptane, 0.374; isobutyl butyrate, 0.320; benzene, 0.91; toluene, 1.00; chlorobenzene, 1.52; ethyl benzoate, 1.55; and  $\alpha$ -chloronaphthalene, 4.30.

J. F. S.

#### Re-examination of the Light Scattered by Gases in respect of Polarisation. I. Experiments on the Common Gases.

LORD RAYLEIGH (*Proc. Roy. Soc.*, 1920, [A], **97**, 435—450. Compare A., 1919, ii, 5).—An improved method by which the residual defect of polarisation in the light scattered by dust-free gases may be measured is described. This quantity has been ascertained for the commoner gases, and the following values of the intensity of weak component polarisation obtained: hydrogen, 3.83; nitrogen, 4.06; air, 5.0; oxygen, 9.4; carbon dioxide, 11.7; nitrous oxide, 15.4 (strong component=100). The author is of the opinion that the error attached to these values is not greater than 5%, and is probably much less.

J. F. S.

#### Re-examination of the Light Scattered by Gases in respect of Polarisation. II. Experiments on Helium and Argon.

LORD RAYLEIGH (*Proc. Roy. Soc.*, 1920, [A], **98**, 57—64. Compare preceding abstract).—The experiments previously described (*loc. cit.*) are continued for helium and argon. Since the scattering due to helium is so slight, special precautions were taken to ensure the purity of this gas, which consisted in allowing the gas to circulate through a layer of charcoal cooled by liquid air immediately before entering the experimental tube. The intensity of the weak component polarisation is found to be argon 0.46, helium <6.5 (strong component=100). The total intensities of light scattered by helium and by air have been compared. The ratio found was 0.0170. Considering the difficulty of the experiment, this is considered to agree within the limit of error with the ratio of the squares of the refractivities, which is 0.0144.

J. F. S.

**Influence of Ammonium Molybdate on the Rotatory Power of Malic Acid.** E. DARMOIS (*Compt. rend.*, 1920, 171, 348—350).—The rotatory power of solutions of malic acid is increased by the addition of ammonium molybdate (compare Gernez, A., 1889, 1147), and the values of  $\alpha_D$  are found to increase at first with the weight of ammonium molybdate and then to become practically constant. If it is assumed that the acid and salt combine to form a compound and the values of  $[\alpha]_D$  are calculated and plotted against the weight of ammonium molybdate added, the curve shows a steep rise to a maximum and then a rapid fall. A solution having the composition corresponding with this maximum, when evaporated, gave a crystalline compound having  $[\alpha] + 219^\circ$  for the yellow ray of mercury, and in addition a very sparingly soluble ammonium molybdate.

W. G.

**The Specific Rotation of Lævulose.** WARREN C. VOSBURGH (*J. Amer. Chem. Soc.*, 1920, 42, 1696—1704).—From measurements of the rotation of lævulose solutions at  $25^\circ$  the concentration varying from 2.6 to 20 grams per 100 c.c., the author deduces the formulæ  $[\alpha]_D^{25} = -(88.50 + 0.145p)^\circ$  or  $[\alpha]_D^{25} = -(88.50 + 0.150c - 0.00086c^2)^\circ$ , where  $p$  is the percentage by weight of the sugar in the solution and  $c$  the number of grams per 100 c.c. Over the temperature range  $15-37^\circ$  the variation of  $[\alpha]_D$  with temperature is given by  $[\alpha]_D^t = [\alpha]_D^{25} + (0.566 + 0.0028c)(t - 25)^\circ$ . The author considers that Ost's results (A., 1891, 1000) are best expressed by  $[\alpha]_D^{20} = -(91.50 + 0.133p)^\circ$ .

For most purposes the values of  $[\alpha]_{\lambda=546\mu}^t$  are given by  $1.1809 [\alpha]_D^t$ , although the coefficient seems to vary very slightly with temperature and concentration.

W. G.

**An Apparatus for using in Photochemical Reactions the Luminous Energy Emitted by an Incandescent Lamp.** V. VOLMAR and C. DUFRAISSE (*Bull. Soc. chim.*, 1920, [iv], 27, 680—681).—A simple arrangement is described by means of which the necessary metallic filament lamp can be introduced into the reaction liquid contained in a glass vessel surrounded by a polished metal jacket, the whole being immersed in a bath by which the temperature can be controlled.

W. G.

**Experimental Decision of the Question of the Radioactivity of all Elements.** G. HOFFMANN (*Ann. Physik*, 1920, [iv], 62, 738—758).—A special very sensitive electroscope capable of photographic registration upon a chronograph and sensitive to 5000 ions per mm., or a deflection of 30 mm. per single  $\alpha$ -particle, has been used to investigate the "natural" radioactivity of common materials. From the range of the  $\alpha$ -particle it can be decided whether the radioactivity is due to known or new radio-elements. The range can be obtained by statistical methods from the observation of the ionisation produced by each  $\alpha$ -particle for a large

number. A discussion of the results obtained for the natural ionisation of a hollow sphere of brass proves that it is not wholly due to radium and its derivatives or to thorium, but in large part to new  $\alpha$ -rays of very short range from a very long-lived radio-element. The material emitted 0.108  $\alpha$ -particle per  $\text{cm}^2$  per hour, with a maximum ionisation of 100,000, corresponding with a range of about 1.8 cm. at *N.T.P.* The period of the element producing it (? copper) must be at least  $1.5 \times 10^6$  times that of uranium, and this agrees with the range found. F. S.

**Reactions in Penetrating Radium Radiation and in Ultra-violet Radiation Filtered by Quartz Glass.** ANTON KAILAN (*Zeitsch. physikal. Chem.*, 1920, **95**, 215—246).—Mixtures of fumaric and maleic acids containing respectively 24, 40, 48, and 64% of maleic acid have been subjected, in 1/50*N*-solutions for 2 to 3000 hours at 6—14°, to the radiation of 80—110 mg. of radium metal through 1 mm. of glass. On the assumption that the decrease in the titre of the solution (5—7%) is due to the formation of acrylic acid, it is found that in all cases but one the maleic acid concentration has increased. This follows from conductivity measurements on the radiated solutions. When the above assumption is approximately true the position of the equilibrium point is much the same when the solution has been radiated with either ultra-violet rays or with radium rays, namely, 72% at 45—50°. Neither by 1632 hours' radiation with the rays from 80 mg. of radium metal, nor by 48 hours' radiation from a quartz mercury lamp, is the density, the refractive index, or the velocity of change into ammonium cyanate, of a normal solution of urea, changed to an extent outside the experimental error. Between 25° and 37° the reaction velocity is increased fourfold for a temperature increase of 10°, which agrees with the measurements of Fawsitt at 90—99° (*A.*, 1903, ii, 15). Similar treatment of aqueous solutions of formic acid changes neither the dissociation constant nor the amount of oxalic acid formation. Both types of radiation induce a decrease in the titre of the solutions, the rate of which decreases as the concentration increases. Only rays with a smaller wave-length than  $0.34 \mu$  are active. A similar treatment of aqueous solutions of benzoic acid produces reducing substances, formic acid and oxalic acid; the velocity of formation of these substances increases as the square of the concentration of the benzoic acid. In this case also only rays smaller than  $0.34 \mu$  are active. The time in which the same effects are brought about by radium rays and by ultra-violet light is in the case of formic acid 270:1 and benzoic acid 7:1.

J. F. S.

**Colouring and Thermoluminescence of Glass produced by Radium Emanation.** S. C. LIND (*J. physical Chem.*, 1920, **24**, 437—443).—A theoretical paper in which the colouring of glass and other materials by radium emanations is discussed. It is shown that all three types of ray have the same effect on the glass, and

that the colouring takes place when pure substances are exposed to the rays. The colour is discharged from both glass and quartz by heating at a temperature at which the former substance commences to soften. Violet glass is slowly decolorised by exposure to sunlight, whilst brown glass is changed to a bright yellow by sunlight or ultra-violet light. When a piece of violet glass is heated at temperatures below  $200^{\circ}$  in the dark it luminesces for a period which is longer the lower the temperature, and after it has ceased to luminesce a further exposure to the radiation is necessary before further luminescence is possible. In this process, however, the violet colour is not affected; the colour only disappears when the temperature is raised to about  $500^{\circ}$ , and there is no luminescence in the temperature interval  $200\text{--}500^{\circ}$ . The more recently the glass has been subjected to the radiation the lower is the temperature at which luminescence occurs; glass which has been recently exposed to radiation commences to luminesce well below the boiling point of water, whilst glass which has been kept for two to three years after exposure only luminesces at  $200^{\circ}$ .

J. F. S.

### **Solubility of Radium Emanation in Organic Liquids.**

ALFRED SCHULZE (*Zeitsch. physikal. Chem.*, 1920, **95**, 257—279).—The solubility of radium emanation has been determined in toluene, ethyl ether, chloroform, acetone, carbon disulphide, ethyl acetate, ethyl alcohol, hexane, water, aniline, and benzene at various temperatures with the object of testing Dolezalek's theory of gas solubility (A., 1910, ii, 184). The results show that this theory represents the experimental facts in a qualitative manner for the solubility of radium emanation, both in normal and associated solvents. As to the quantitative aspect of the case it is impossible to draw any conclusions because the amount of radium emanation dissolved is small, and measurements are thereby rendered very inexact. Despite this, it is possible to obtain trustworthy data of the solubility from measurements of the vapour tension of the emanation if the correct molecular weight of the solvent is brought into the calculations. On the other hand, it is possible to deduce directly, from the course of the solubility curve, trustworthy values of the molecular weight of the solvent and so gain an insight into the molecular condition of liquids.

J. F. S.

### **Geiger-Nuttall Equation.**

GERHARD KIRSCH (*Physikal. Zeitsch.*, 1920, **21**, 452—456).—Application is made of the hypothesis that the atomic nucleus consists exclusively of helium and hydrogen nuclei with electrons, and of the Geiger-Nuttall relation in the form given by Lindemann (A., 1915, ii, 720), to deduce regularities in the disintegration series of radium and thorium. From these regularities, applied to the actinium series, conclusions are formed as to the atomic weights of these elements. An attempt is also made to show that there are three radioactive disintegration series.

J. R. P.

**$\alpha$ -Ray Rules.** HANS TH. WOLFF (*Physikal. Zeitsch.*, 1920, **21**, 393—396).—The rule  $\log R = x \log (K - s) + y$ , where  $\log R$  is the common logarithm of the range of the  $\alpha$ -ray in cm. at *N.T.P.*,  $x$  a positive, and  $y$  a negative constant,  $K$  a constant, and  $s$  the order of the change in the disintegration series in which the  $\alpha$ -particle is expelled, counting for the first  $s=0$ , the second  $s=1$ , and so on, represents the ranges of the  $\alpha$ -rays of all four series approximately, the uranium series being considered two, from uranium-*I* to radium, and from radium emanation to radium-*C'*, polonium, actinium-*X*, actinium-*C*, and thorium-*C* being exceptions. The values of  $x$  and  $y$  change for each of the four series, and the value of  $K$  is one-fourth of the atomic weight for the thorium and first part of the uranium series, 58 and 60, and 54 and 55 for the second part of the uranium series and for actinium respectively.

Discussing this relation theoretically, by the aid of the quantum relation it is deduced that the  $\alpha$ -particle is travelling in an orbit of radius  $\rho$  in the nucleus, given by the relation  $\rho = (K - s)^{-2/3}$  const.

F. S.

**Electron Affinity of the Sulphur Atom.** M. BORN and ELIZABETH BORMANN (*Zeitsch. Physik*, 1920, i, 250—255).—X-Ray measurements of the crystal lattice of zinc sulphide and application of the lattice theory lead to the value of 50 for the electron affinity of the sulphur atom. This value corresponds with an ionisation potential of 2.16 volts.

CHEMICAL ABSTRACTS.

**Conductivity and Frequency.** E. D. EASTMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 1648—1655).—It is suggested that the conductivity of solutions of electrolytes is smaller at zero frequency than at any frequency in a certain range immediately above zero. Measurements of *N*-potassium chloride and sulphuric acid of maximum conductivity are described, and it is shown that the difference between direct current conductivities and those at 1000 cycles does not exceed 0.02—0.03%, but the difference lies in the direction expected. The conductivity of *N*-potassium chloride at 25° given by Kohlrausch is confirmed within 0.1%.

J. F. S.

**The Thermoelectric Power of Pure Metals.** H. PÉLABON (*Ann. Physique*, 1920, [ix], **13**, 169—187).—From a study of the variation of the thermoelectric power with temperature, at temperatures above the melting point of one metal of the couples, it is shown that the thermoelectric power of pure metals varies continuously with the temperature, there being no discontinuity at the melting point. For the metals in the liquid state the thermoelectric power is a linear function of the temperature, at least for lead, tin, and bismuth. For antimony the results are not so regular.

W. G.

**Theory of Electrocapillarity. I. and II.** ALEXANDER FRUMKIN (*Phil. Mag.*, 1920, [vi], **40**, 363—375, 375—385).—I. Gouy's theory



(A., 1917, ii, 291) that the superficial electric charge is zero at the maximum of the electrocapillary curve, but that there may be a potential difference between the mercury and the solution, due to adsorbed ions, is confirmed. The ordinary equation of the electrocapillary curve  $\partial\gamma/\partial\psi = \epsilon$  is replaced by  $\partial\gamma/\partial\psi = \epsilon + \Gamma_{\text{Hg}}F$ , where  $\gamma$ =surface tension,  $\epsilon$ =electric charge on unit surface of the mercury,  $\psi$ =potential difference between a decinormal calomel electrode and the mercury in the solution,  $\Gamma_{\text{Hg}}$  = adsorption excess of mercury in gm. equiv. per sq. cm. of dividing surface,  $F=96,540$  coulombs. The results are incompatible with Nernst's theory, based on electrolytic solution pressure, since the potential difference between solution and mercury is not necessarily connected with exchange of ions of mercury, but may be caused solely by adsorbed layers of anions and cations.

II. A modification of Gibbs's adsorption equation is deduced, in which separate account is taken of the adsorption of the anion and the cation, and is used to calculate the horizontal distance between the ascending and descending branches of electrocapillary curves at different concentrations (Gouy, *loc. cit.*). The results are in fair agreement with the observed values, but the calculation of the maximum is less satisfactory.

J. R. P.

**Activities of Ions in Aqueous Solutions of some Strong Electrolytes.** FREDERICK H. GETMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 1556—1564. Compare Noyes and MacInnes, this vol., ii, 345).—The *E.M.F.* of cells of the type  $\text{Hg}, \text{HgCl} | \text{MCl}(c_1) || \text{MCl}(c_2) | \text{HgCl}, \text{Hg}$ , in which M is sodium, potassium, or hydrogen, and in which the concentrations varied over wide limits, have been measured at 25°. In addition, the two cells  $\text{Hg}, \text{HgCl} | 0.1N\text{KCl} || 0.1N\text{NaCl} | \text{HgCl}, \text{Hg}$  and  $\text{Hg}, \text{HgCl} | 0.1N\text{KCl} || 0.1N\text{HCl} | \text{HgCl}, \text{Hg}$  have also been carefully measured, and from the results the activities of the ions have been calculated. The results show, as in the work of Beattie and MacInnes (this vol., ii, 467), that the conductivity-viscosity ratio does not afford a trustworthy measure of the activity of the ions of strong electrolytes. Furthermore, the marked increase in the activity-coefficient of hydrochloric acid, which occurs beyond 0.5*N*, proves conclusively that this quantity cannot be proportional to the degree of ionisation.

J. F. S.

**Electromotive Behaviour of Aluminium.** I. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 876—881).—A theoretical paper in which an explanation of the valve action of aluminium is put forward. The ennobling of the aluminium potential on anodic polarisation occurs as follows. During the withdrawal of electrons from the metal, represented by  $3\theta_s$ , aluminium ions pass into solution,  $\text{Al}_s''' \rightarrow \text{Al}_l'''$ , and because this heterogeneous equilibrium is established instantaneously the reaction  $\text{Al}_s \rightarrow \text{Al}_s''' + 3\theta_s$  proceeds with a very small velocity, so that the metal becomes poorer in ions and electrons. In consequence of this the potential of the metal becomes more positive, as is seen from the

equation  $E = 0.058/v \cdot \log L_M/M_L - 2.8$ , because in this case  $L_M$  becomes smaller. Since the metal is inert the discharge potential of oxygen will soon be reached and oxygen will be liberated, which in certain circumstances may lead to the formation of an adherent coating of oxide on the metal. This coating gives rise to a certain resistance which may rise to a considerable value with increasing thickness. The assumption, however, that the resistance of such a coating should be different for different directions of the current is not justifiable, so that the sudden decrease of resistance on reversal of the current must be due to another cause. The small quantity of oxygen absorbed by the metal is a negative catalyst towards the setting up of the internal metal equilibrium. Hence the metal surface, being very poor in ions and electrons, passes into a metalloid condition, that is, it possesses small conductivity. Hence on anodic disturbance the aluminium surface becomes a metal layer of great resistance, and this coating is in turn surrounded by another of alumina. On reversal of the current the hydrogen liberated removes the absorbed oxygen, and the aluminium surface is transformed with great velocity into a condition of internal equilibrium, that is, the coating of great resistance is changed into one of negligible resistance. Hence the resistance remaining when aluminium is changed from anode to cathode is chiefly the resistance of the alumina.

J. F. S.

**Ignition of Gases at Reduced Pressures by Impulsive Electric Sparks.** W. M. THORNTON (*Phil. Mag.*, 1920, vi, 40, 345—356).—Ignition by impulsive sparks is, on the whole, more difficult at low pressures, in this differing from ignition by hot wires. In hydrogen and methane the increase of difficulty takes place by well-marked steps or stages. In ethane or propane this does not occur, but there is an oscillation of the curve, found also in hydrogen and carbon monoxide. This appears to be associated with the temperature of the sparking point during the passage of the spark. It has been shown previously (A., 1914, ii, 524, 834; 1915, ii, 734) that at pressures well above atmospheric sudden changes of inflammability occur when ignition is by impulsive sparks or condenser discharge. It is now found that there are such steps at reduced pressures, and that there is a close agreement between the partial pressures corresponding with the points at which oxygen has ratios to the mass of the combustible gas expressed by successive natural numbers, and the pressures at which sudden changes of inflammability occur.

J. R. P.

**Dye Cells.** E. STAECHELIN (*Zeitsch. physikal. Chem.*, 1920, 94, 542—591).—The change in *E.M.F.* produced in cells containing various fluorescent dyes on illumination with a 3000 candle-power half-watt lamp has been measured against a *N*-calomel electrode. Rhodamine-*B*, rhodamine-3*B*, sodium eosin, quinine sulphate, tetrachlorofluorescein, the phosphine dye, the sodium salts of  $\beta$ -naphthylamine-6:8- and 5:7-disulphonic acids,

and resorufin, were all measured both alone in solution and in the presence of oxidising and reducing agents, such as acetaldehyde, formaldehyde, oxalic acid, ferrous sulphate, iodine, vanadium tetroxide in sulphuric acid, ferric sulphate, hydrogen, oxygen, quinol, and other substances, such as potassium chloride, iodide, and sodium carbonate. It is shown that the Becquerel effect takes place in both directions, and its dimensions and direction depend on the presence of reducing and oxidising agents. The behaviour of all the cells examined can be explained by the assumption of a hidden oxygen-hydrogen photolysis.

J. F. S.

**Metastability of the International Weston Element and its Unsuitability as an [Electrical] Tension Normal.** ERNST COHEN and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1920, **95**, 285—304).—The international Weston element with a 12.5% cadmium amalgam, which was recommended by the international conference on electrical standards and units (Washington, 1908), does not fulfil the demands which are required from a standard of electromotive force. This is because the results of Cohen (A., 1900, ii, 702), Bijl (A., 1903, ii, 6), and F. E. Smith (*Collected Researches Nat. Phys. Lab.*, 1910, **6**, 137) on the composition of the element have not been sufficiently taken into account. This element at temperatures below 12° is a metastable system, which may spontaneously become stable with a noticeable change in the *E.M.F.* amounting to about 6 millivolts at 0°, and for this reason is unsuitable as a standard. The temperature formula recommended by the conference for use between 0° and 40° with this element refers to elements which are metastable up to 12° and stable above this temperature. The Weston element is to be replaced by an element containing 8% cadmium amalgam as recommended by Cohen and Kruyt (A., 1910, ii, 178, 259), which is stable from a few degrees below zero to 40°. The temperature formula mentioned above is strictly applicable to elements containing 8% cadmium amalgam from 0° to 40°, and may be applied to all such elements which are stable over this range of temperature. The Weston elements supplied by the Weston Company containing 12—13% cadmium amalgam are also unstable below 12°, and are also unsuitable as normals of electromotive force.

J. F. S.

**Moving Striations in Neon and Helium.** F. W. ASTON and T. KIKUCHI (*Proc. Roy. Soc.*, 1920, [A], **98**, 50—56).—When the flash of an ordinary spectrum tube containing neon or helium is analysed by a rotating mirror it is found to consist of an extremely short flash followed by a flame or arc, and that the latter consists of bright striations travelling from anode to cathode. The velocity of these striations is found to be about 50,000 cm./sec. in neon and 100,000 cm./sec. in helium. These values are a limiting case, and the velocity varies with varying conditions, such as pressure, diameter of tube, and temperature. Neither air nor hydrogen

showed moving striations in capillary tubes, but in a tube 1.6 mm. wide both developed stationary striations at 1 mm. to 2 mm. pressure.

J. F. S.

**Variation of Magnetic Susceptibility during Allotropic Transformations and Melting of some Substances.** TORAJIRŌ

ISHIWARA (*Sci. Rep. Tohoku Imp. Univ.*, 1920, 9, 233—241).—

The magnetic susceptibility of five weakly magnetisable substances was examined over considerable ranges of temperature in a modified torsion balance apparatus which could be exhausted or filled with inactive gas. Water was used as the standardising substance of the apparatus, its specific susceptibility being accurately known. Silver bromide is diamagnetic. On cooling, its susceptibility is fairly constant down to 200°, below which there is a slight decrease but no discontinuity in passing through the melting point. Silver chloride is also diamagnetic, the susceptibility increasing with rising temperature, with no discontinuity during fusion. The diamagnetic susceptibility of sulphur shows no discontinuity at the transformation from rhombic into monoclinic crystals, and the curves give no definite indication of fusion, but the transformation in the liquid phase at 160—170° is accompanied by a decrease of about 2% in diamagnetism, after which the susceptibility is again constant. There are indications of a reversible magnetic change at about 80° which may be due to the presence of an amorphous sulphur. The diamagnetic susceptibility of zinc shows a sudden decrease of about 4% at the melting point with a linear decrease above and below this point. Aluminium is paramagnetic, and its susceptibility is constant over a range of 100° below its melting point. During fusion it increases by about 2% and then remains constant.

T. H. B.

**Molecular Theory of the Paramagnetism of Solid Salts.**

OTTO STERN (*Zeitsch. Physik.*, 1920, i, 147—153; from *Chem. Zentr.*, 1920, iii, 297).—Curie's law,  $\chi T = \text{const.}$  (where  $\chi$  is the susceptibility and  $T$  the absolute temperature), has been applied by Weiss to solid substances on the basis of Langevin's theory and on the assumption that here also the molecules, as carriers of the elementary magnets, are able to rotate freely. Since, however, doubts have been cast on this assumption, Weiss endeavoured to show later that it is not really essential if the condition is fulfilled that the molecules are attached to stable equilibrium positions or, in consequence of temperature changes, oscillate round these positions, provided only that the orientation of these equilibrium positions does not occur in any preferential direction (amorphous substances and crystalline powders). The detection of an error in Weiss' calculations has led the author to recalculate the entire subject. He is led to the diametrically opposite conclusion that the susceptibility of such a substance is independent of the temperature to a first approximation, and only as a second approximation decreases somewhat but only very slightly with increasing tempera-

ture—a result which could be predicted without calculation. Curie's law cannot therefore be valid for molecules oscillating round an equilibrium position, but only for such as are able to rotate freely. Since the molecules in a crystal certainly do not conform to this condition and Curie's law is known to be valid, the author is led to the conclusion that the molecules cannot be regarded as the carriers of the magnetic moment, and that this function is probably performed by the ions.

H. W.

**Volume Change Produced on Diluting Concentrated Solutions or Mixing Two Liquids.** [FRL.] IRENE D. GÖTZ (*Zeitsch. physikal. Chem.*, 1920, **94**, 181—209).—The thermal expansion of ethylene dichloride, benzene and ethyl ether under a pressure of 420 and 350 atms. respectively has been determined over the range 0—40°; the volume change is represented by the following equations: ethylene dichloride,  $v = 0.78025(1 + 0.0011109t + 0.000001696t^2)$ ; ethyl ether,  $v = 1.35786(1 + 0.0015006t + 0.00000437t^2)$ ; benzene,  $v = 1.11250(1 + 0.0011715t + 0.000000155t^2)$ . The thermal expansion of mixtures of ethyl ether—ethylene dichloride and ethyl ether—benzene of various concentrations has been determined and found to be the same as that of ethyl ether under definite external pressure. These pressures were proportional to the concentration of the ethylene dichloride up to 49.875% and to that of the benzene up to 100%. Making use of Tammann's law of concentrated solutions, the contraction on mixing a concentrated solution of ethylene dichloride in ethyl ether with ethyl ether has been calculated and the values found to be very near the experimentally determined value. The contraction on mixing ethyl ether with benzene has been calculated on the assumption that two liquids only differ from one another and from their mixture in respect of their internal pressure, and the volume change depends only on the total pressure. The calculated values are very nearly those determined experimentally, except in a few cases.

J. F. S.

**Graphic Representation of the Characteristic Equation.** R. MOILLER (*Physikal. Zeitsch.*, 1920, **21**, 457—463).—The magnitude  $y = pv^2/T$  is plotted as ordinate against the density or the reciprocal of the absolute temperature as abscissæ. The resulting diagrams for different characteristic equations are discussed.

J. R. P.

**Theory of the Solid State of Aggregation.** A. VAN DER WERTH (*Zeitsch. physikal. Chem.*, 1920, **95**, 129—138).—A theoretical paper in which a number of properties of solids are treated mathematically. It is shown that the specific heat and the mechanical solidity bear a simple relationship to one another. Both quantities depend on the molecular attraction, and furnish a measure of the resistance with which a substance opposes any force which tends to disrupt it. This resistance is termed the "work of expan-

sion," and may be calculated from the modulus of elasticity and also from the specific heat and the thermal expansion. The following relative values have been calculated for the lengthening by 1/100 mm. of the following substances, from the specific heat values: Al, 8.05; Pb, 5.2; Cd, 8.07; Fe, 31.25; Au, 18.08; Cu, 20.37; Na, 0.168; Ni, 29.7; Pd, 24.45; Pt, 32.7; Ag, 12.7; Bi, 9.41; Zn, 9.67; and Sn, 7.1. The values calculated from the modulus of elasticity in many cases differ very much from the above values. The method adopted in the above calculations permits of qualitative conclusions being drawn in connexion with the mechanical properties of solid substances from simple thermal data.

J. F. S.

**An Electrical Adiabatic Calorimeter and its Use in the Determination of the Specific Heat of Solutions of Cadmium Sulphate.** ERNST COHEN and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1920, **95**, 305—327).—The construction of an adiabatic calorimeter is described, which in its chief points follows closely the adiabatic calorimeter of Richards (A., 1908, ii, 806). The main point of difference lies in the heating of the liquid in the protecting jacket. Richards changed the temperature of the jacket by neutralising sodium hydroxide solution at a measured rate, whilst in the present case the change in temperature is effected by the passage of a known amount of electrical energy into the water in the surrounding jacket. An accuracy of 0.5 per 1000 is claimed for the results obtained with this instrument. The specific heat of solutions of cadmium sulphate from 1.89% to 44.63% (by weight) has been determined, and values obtained which steadily fall from 0.9763 with the most dilute solution to 0.5725 with the most concentrated. The results are compared with the values obtained by Berthelot-Thomsen and found to differ by quantities varying from 1/7000 to 36/6000.

J. F. S.

**Indirect Method of Determining the Specific Heat of Dilute Solutions with Preliminary Data Concerning Hydrochloric Acid.** THEODORE W. RICHARDS and ALLAN W. ROWE (*J. Amer. Chem. Soc.*, 1920, **42**, 1621—1635).—The specific heat of a dilute solution can be determined indirectly from the difference in the heat developed on diluting a known concentrated solution to a solution of the desired strength at two temperatures. The method is based on Kirchhoff's law,  $K_M - K'_M = (U' - U)/\Delta\theta$ , in which  $K_M$  and  $K'_M$  are the molecular heat capacities of the two substances,  $U$  and  $U'$  the respective total energy changes, that is, the heats of dilution at  $\theta$  and  $(\theta + \Delta\theta)$ . This method has been carried out with the utmost care for solutions of hydrochloric acid. The following molecular heats of dilution have been obtained for 20°:  $\text{HCl}, 10\text{H}_2\text{O} + 15\text{H}_2\text{O}$ , 714 cal.;  $\text{HCl}, 10\text{H}_2\text{O} + 40\text{H}_2\text{O}$ , 949;  $\text{HCl}, 10\text{H}_2\text{O} + 90\text{H}_2\text{O}$ , 1082;  $\text{HCl}, 20\text{H}_2\text{O} + 80\text{H}_2\text{O}$ , 480;  $\text{HCl}, 10\text{H}_2\text{O} + 190\text{H}_2\text{O}$ , 1161;  $\text{HCl}, 20\text{H}_2\text{O} + 180\text{H}_2\text{O}$ , 549;  $\text{HCl}, 10\text{H}_2\text{O} + 390\text{H}_2\text{O}$ , 1219;  $\text{HCl}, 10\text{H}_2\text{O} + 790\text{H}_2\text{O}$ , 1247. The following specific heats, for which

an accuracy of about 0.05% is claimed, have been obtained:  $\text{HCl}, 10\text{H}_2\text{O}$ , 0.752;  $\text{HCl}, 20\text{H}_2\text{O}$ , 0.849;  $\text{HCl}, 25\text{H}_2\text{O}$ , 0.8776;  $\text{HCl}, 50\text{H}_2\text{O}$ , 0.9320;  $\text{HCl}, 100\text{H}_2\text{O}$ , 0.9634;  $\text{HCl}, 200\text{H}_2\text{O}$ , 0.9812; and  $\text{HCl}, 400\text{H}_2\text{O}$ , 0.9905. This method of determining specific heats is to be recommended because it is easier to measure two heats of dilution than one direct specific heat.

J. F. S.

### Variation of the Specific Heat of a Gas with Temperature.

GEORGE W. TODD (*Phil. Mag.*, 1920, [vi], **40**, 357—362).—It is shown that continuous change of specific heat with temperature is not inconsistent with the theory of equipartition, and that the data for hydrogen are explained by the theory of equipartition as well as by the quantum hypothesis. It is assumed that gas molecules have three degrees of freedom so long as their velocities are below a critical value; above this value collisions result in the acquisition of further degrees of freedom.

J. R. P.

### Specific Heat of Saturated Vapours at Low Temperatures.

E. ARIÈS (*Compt. rend.*, 1920, **171**, 456—458).—A criticism of Bruhat's work (this vol., ii, 528), in which the author reaffirms his own views on the subject (*A.*, 1917, ii, 192).

W. G.

**Third Law of Thermodynamics and the Entropy of Solutions and of Liquids.** GILBERT N. LEWIS and G. E. GIBSON (*J. Amer. Chem. Soc.*, 1920, **42**, 1529—1533).—A theoretical paper in which the Nernst third law of thermodynamics and the entropy of liquids and solutions are considered. The third law of thermodynamics is restated as follows: "If the entropy of each element in some crystalline form is taken as zero at the absolute zero, the entropy of any pure crystal at the absolute zero is zero and the entropy of any other substance is greater than zero." It is, however, likely that the difference between the entropy of a pure substance in the crystalline state and in any amorphous state may, in many cases, prove to be very small.

J. F. S.

**Entropy Changes at Low Temperatures. I. Formic Acid and Carbamide. A Test of the Third Law of Thermodynamics.** G. E. GIBSON, W. M. LATIMER, and G. S. PARKS (*J. Amer. Chem. Soc.*, 1920, **42**, 1533—1542).—The specific heat of formic acid and of carbamide has been determined at a large number of temperatures from  $71.0^\circ \text{K}$  to  $300.3^\circ \text{K}$ . For formic acid the following values have been obtained:  $71.0^\circ \text{K}$ ,  $C_p$  per gram = 0.157;  $90.3^\circ \text{K}$ ,  $C_p = 0.182$ ;  $250.5^\circ \text{K}$ ,  $C_p = 0.344$ ; and  $291.5^\circ \text{K}$ , 0.510; for carbamide the results include:  $86.4^\circ \text{K}$ ,  $C_p = 0.239$ ;  $107.5^\circ \text{K}$ ,  $C_p = 0.259$ ;  $244.2^\circ \text{K}$ ,  $C_p = 0.382$ ; and  $300.3^\circ \text{K}$ ,  $C_p = 0.460$ . From these values the free energy and entropy have been calculated, and the following values, which are in keeping with the third law of thermodynamics (see preceding abstract), are obtained: Formic acid,  $S_{281.5^\circ} = 4.72$  per atom, and  $S_{281.5^\circ} = 4.86$  per atom or 24.30 per mol.; the entropy of fusion is 8.60.

$S_{298}^{\circ}$ (liquid) = 34.2. The free energy of formation from the elements is -85370 cal., and from carbon monoxide and water 3415 cal., both at 298° K. Carbamide,  $S_{298}^{\circ} = 41.0 \pm 2.0$ , and the free energy of formation from the elements is  $\Delta F_{298}^{\circ} = -48,992$  cal. J. F. S.

**Entropy Changes at Low Temperatures. II. Ethyl and Propyl Alcohols and their Equimolecular Mixture.** G. E. GIBSON, G. S. PARKS, and W. M. LATIMER (*J. Amer. Chem. Soc.*, 1920, **42**, 1542—1550. Compare preceding abstract).—The specific heat of ethyl alcohol, propyl alcohol, and an equimolecular mixture of the two has been determined for the liquids, crystalline solids, and the glasses at temperatures from 78.5° K to 274.6° K. The heat of fusion of ethyl alcohol at the melting point 156.2° K is found to be 24.0 cal. per gram or 123 cal. per gram-atom. The molecular heat capacities are: ethyl alcohol, 268.7° K, 24.39; 198.3° K, 21.10; 90.0° K, 12.80; and 86.0° K, 12.15; propyl alcohol, 268.7° K, 30.96; 198.3° K, 26.67; 90.0° K, 15.17; and 86.0° K, 14.47, whilst the values for the equimolecular mixture at the same temperatures are 27.72, 23.83, 13.90, and 13.21 respectively. From the data it appears probable that the entropy of the equimolecular mixture is not zero at the absolute zero. Assuming the validity of the third law of thermodynamics to the process ethyl alcohol (supercooled)  $\rightarrow$  ethyl alcohol (crystalline)  $\Delta S_{156.2}$  has been calculated by two methods. The difference (per gram-atom) between the results obtained is 0.12 cal. per degree or 20 cal. at 156.2° K. By means of the third law of thermodynamics the free energy of ethyl alcohol has been calculated to  $F_{298}^{\circ} = -43,000$  cal. J. F. S.

**Space-filling and Ionic Mobility.** RICHARD LORENZ (*Zeitsch. Elektrochem.*, 1920, **26**, 383—384).—The author refers to the work of H. Kauffmann (this vol., ii, 16) as of importance in the extrapolation of electric conductivities to the limiting value, but differs from him in considering the boiling points as corresponding states for liquids. J. R. P.

**Some Little-noted Sources of Error in Boiling-point Determinations under Reduced Pressure.** C. VON RECHENBERG and E. BRAUER (*Zeitsch. physikal. Chem.*, 1920, **95**, 184—214).—A large number of experiments on the determination of boiling points under reduced pressure are described. It is shown that the temperature of the vapour in the boiling tube decreases from the bottom upwards, in individual cases as much as 20°. The electrically determined temperature measurements of Hansen (A., 1910, ii, 827) show that there is a more rapid fall of temperature between the surface of the boiling liquid and a height 1—2 cm. above it than elsewhere, which may be explained by the presence of fine drops of superheated liquid carried upward by the vapour. The temperature gradient in the upper half of the boiling tube is regular, and occasionally greater than in the lower half. The temperature fall therefore increases from the bottom upward, and this is true in all cases



and with all variations of heating and temperature of the mantle. With increase in the heating, that is, with increase in the amount of vapour evolved, the temperature increases at all points in the boiling tube, but in general the temperature gradients and temperature differences do not change to any marked extent. The temperature of the surrounding mantle influences the temperature of the vapour to a marked extent. The following conditions are recommended for the determination of boiling points by the dynamic method. The boiling flask may be of glass or metal; in the latter case a flattened bottom is preferable, whilst in the case of glass a second neck carrying a capillary tube is advantageous. The neck of the flask should be surrounded with a vapour mantle; the boiling tube must be at least 20 mm. wide, the neck and condenser tubes 15 mm. wide. The thermometer bulb must be placed at least 50 mm. above the level of the boiling liquid and the whole of the mercury thread should be in the vapour. Pressure measurements should be made on the boiling tube. The manometer should have a limb 15 mm. wide and must be perfectly vertical, and pressures of less than 5 mm. should not be measured in this way. The velocity of distillation must never be greater than one drop per second, and no temperature or pressure readings should be made until at least 10 c.c. have distilled over.

J. F. S.

**The Boiling Points, Critical Temperatures and Pressures in Homologous Series.** MAURICE PRUD'HOMME (*J. Chim. physique*, 1920, 18, 94—102).—In a homologous series the value of  $T_1/T_c$  increases from one member to the next higher in the series,  $T_1$  being the absolute boiling point and  $T_c$  the absolute critical temperature.  $(T_c - T_1)$  increases or decreases similarly according to the particular series, and  $T_1/T_c$  divided or multiplied by  $(T_c - T_1)$  is a constant for each series.

The difference in the critical temperatures of two adjacent members in the series of paraffin hydrocarbons is given by  $\Delta = 210/T_c^{0.0135T/\sqrt{T_c}}$ .

For isomeric esters,  $(T_c - T_1)/(T_c - T_2)$  is a constant, where  $T_1$  and  $T_2$  are the absolute boiling points at two different pressures. Further,  $(T_c - T_1)$  is an exponential function of the critical pressure.

The introduction of any one of the halogen elements into a hydrocarbon gives for  $T_1/T_c$  and  $T_c/(T_c - T_1)$  constant values independent of the nature of the halogen.

W. G.

**Ulrich Dühring's Law of Boiling Points at Similar Pressures. The Zero Point of Vaporisation.** C. von RECHENBERG (*Zeitsch. physikal. Chem.*, 1920, 95, 154—183).—A theoretical paper in which Dühring's rule is examined by means of a large amount of previously published vapour pressure data. It is shown that this rule may be restated as follows. The saturation temperatures, for equal pressures of pure uniform chemical substances having similar vapour-pressure curves, change in the same way if the compounds during vaporisation do not change their

constitution, that is, neither dissociate nor associate, and when the vapour is entirely unimolecular. The author postulates a minimum temperature at which a substance ceases to exert a vapour pressure; this is the temperature at which vapour ceases to be capable of existence, and is termed the zero of vaporisation; it differs for every substance, and if it is found experimentally for a single substance can be calculated for all others by Dühring's rule. The vaporisation zero of hydrogen is the same as the absolute zero, as follows from the vapour-pressure determinations of Travers, Senter, and Jaquerod (A., 1903, ii, 9). Using this value, those of about fifty other substances have been calculated. The values of the more common substances are: oxygen,  $-243.91^{\circ}$ ; carbon dioxide,  $-171.49^{\circ}$ ; ammonia,  $-161.83^{\circ}$ ; chlorine,  $-182.29^{\circ}$ ; ethyl ether,  $-146.73^{\circ}$ ; ethyl alcohol,  $-91.96^{\circ}$ ; benzene,  $-129.71^{\circ}$ ; water,  $-87.84^{\circ}$ ; benzoic acid,  $+1.73^{\circ}$ ; glycerol,  $+27.85^{\circ}$ ; and sulphur,  $6.57^{\circ}$ .  
J. F. S.

**Vapour Pressure Equation.** CYRIL H. MEYERS (*Phil. Mag.*, 1920, [vi], 40, 362—363).—The equation of Todd and Owen (A., 1919, ii, 495) is criticised adversely.  
J. R. P.

**Approximation Formulæ for Univariant Systems.** J. A. VAN LIEMPT (*Zeitsch. anorg. Chem.*, 1920, 111, 280—288).—A theoretical paper in which the author deduces formulæ by which the vapour pressure and sublimation pressure in univariant systems may be approximated from known data. The formulæ are based on the Clapeyron formula,  $dp/dT = Q_v/(v_g - v_l)T$ , and have the form  $\pi = -0.2184k_1T_k\tau + 0.2184k_1$ , in which  $k_1$  is the Trouton constant (21),  $T_k$  the boiling point, and  $\tau = 1/T$ , the temperature under discussion; supplying the value of the constants, the formula becomes  $\pi = -4.59T_k\tau + 4.59$ . This formula holds in the region of the critical point if it is written in the form  $\log p_{\text{crit}} = -4.59T_k/T_{\text{crit}} + 4.59$ . The sublimation pressure is given by  $\pi = -(2.95T_s + 4.59T_k)\tau + 7.53$ .  
J. F. S.

**Liquefaction of Air and the Characteristic Equation.** K. SCHREBER (*Physikal. Zeitsch.*, 1920, 21, 430—433).—A discussion of the Joule-Kelvin effect leads to the characteristic equation  $v^3 - (RT/p - a/T + c)v^2 - bR^2T = 0$ , instead of van der Waals's equation  $v^3 - (RT/p + b)v^2 - av/p + ab/p = 0$ .  
J. R. P.

**Heat of Reaction.** WALTHER JANKOWSKY (*Zeitsch. Elektrochem.*, 1920, 26, 385—391).—The energy-content of a body consists of heat and potential energy, which are interconvertible. Nernst's theorem is deduced from this assumption. Kirchhoff's equation for the dependence of heat of reaction on temperature, and Nernst's use of the equation, are said to be incorrect. The author believes that affinity is independent of temperature.  
J. R. P.

**Heats of Combustion of Benzene, Toluene, Aliphatic Alcohols, cycloHexanol, and other Carbon Compounds.**

THEODORE W. RICHARDS and HAROLD S. DAVIS (*J. Amer. Chem. Soc.*, 1920, **42**, 1599—1617).—The heat of combustion of a number of carbon compounds has been most carefully determined, and the following values obtained in 18° calories per gram: sucrose, 3943; benzoic acid, 6320; naphthalene, 9614; benzene, 10,014; toluene, 10,155; *tert.*-butylbenzene, 10,434; cyclohexanol, 8882; diisooamyl, 11,339; methyl alcohol, 5326; ethyl alcohol, 7101; propyl alcohol, 8033; *n*-butyl alcohol, 8615; and *isobutyl* alcohol, 8599. The heat effect for the addition of CH<sub>2</sub> in alcohols, and in the side-chains of aromatic hydrocarbons, is 648 kilojoules or 153.5 Cal., whilst that for the addition of CH<sub>2</sub> in the benzene ring is 638 kilojoules.

J. F. S.

**Calculation of Theoretical Heats of Solution.** H. VON

STEINWEHR (*Zeitsch. physikal. Chem.*, 1920, **94**, 6—24).—A theoretical paper in which the calculation of the theoretical or fictitious heat of solution is considered. It is shown that the two most important methods for calculating this quantity, as put forward by Cohen and Bruins (*A.*, 1918, ii, 297), are only possible in the case of anhydrous salts. The method applicable to hydrates, which can also be applied to anhydrous salts, was deduced by W. Jaeger (*Ber. Deut. physikal. Ges.*, 1901, **3**, 48), and has now been developed without the objections which were raised to Jaeger's method, and it has been used to calculate the fictitious heat of solution of CdSO<sub>4</sub>.8/3H<sub>2</sub>O at 4° and the value -182.85 cal. obtained. The formula for calculating the temperature-coefficient of the fictitious heat of solution given by Cohen and Bruins (*loc. cit.*) is shown to be incorrect, and corrected formulæ have been deduced for the cases applying to hydrates and anhydrous salts. The probable course of the fictitious heat of solution of CdSO<sub>4</sub>.8/3H<sub>2</sub>O, with temperature changes, has been calculated from the values calculated for -7.3°, 4°, and 18°. It is also shown that by making use of a modification of Kirchhoff's formula for the heat of solution, the fictitious heat of solution and the difference between the total energy of elements, may be calculated both for the conditions with and without solid phase if the dependence of the tension of aqueous vapour of the solution on the dilution of the solution and the temperature-coefficient of the solubility of the salt are known. These formulæ hold for both anhydrous salts and hydrates.

J. F. S.

**Theory of Binary Mixtures. VI. Compressibility of Binary Mixtures.** F. DOLEZALEK and F. SPEIDEL (*Zeitsch. physikal. Chem.*, 1920, **94**, 72—110).—The theory of the compressibility of binary mixtures is developed in connexion with the

author's theory of binary solutions (this vol., ii, 32). The compressibility of the binary mixtures, benzene-ethylene dichloride, ethyl ether-chloroform, and benzene-carbon tetrachloride has been determined at 24.6° for all possible concentrations up to a pressure

of 600 kilo./sq. cm. The compressibility curve for mixtures of benzene and ethylene dichloride is a straight line at all pressures, which indicates, in keeping with previous vapour-pressure measurements (*loc. cit.*), that both substances are unimolecular and that the compressibility is additive at all concentrations. The compressibility curve for mixtures of ethyl ether and chloroform at lower pressures is strongly convex to the abscissæ axis; consequently there is a strong deviation from simple additivity in the compressibility of these substances. If the amount of complex formation between these substances, previously found from vapour-pressure measurements, is taken into account, the curve becomes a straight line and exact additivity is obtained over the whole range of concentrations. With increasing pressure, in accordance with the theory, the curvature becomes less, and eventually it becomes concave to the abscissæ axis. Mixtures of benzene and carbon tetrachloride exhibit at lower pressures a strongly concave compressibility curve, which is in keeping with the previous vapour-pressure measurements. If the formation of double molecules by the benzene is taken account of, the compressibility for all concentrations becomes additive, and a straight line curve is obtained. With increasing pressure the curve becomes convex, as is demanded by the theory. J. F. S.

**Application of the Law of Limiting Densities to Easily Liquefiable Gases and the Atomic Weight of Sulphur.**

EUGÈNE WOURTZEL (*J. Chim. physique*, 1920, **18**, 142—150).—In the light of Guye's recent work (A., 1919, ii, 318), the author has revised certain of his previous calculations (A., 1913, ii, 771), and in particular calculations of the results obtained by Jaquero and Scheuer on the compressibility of sulphur dioxide. From these calculations he deduces an atomic weight of sulphur,  $32.059 \pm 0.006$ .

W. G.

**The Viscosimeter as a means of Determining Density.**

J. HOLKER (*J. Path. Bact.*, 1920, **23**, 185—187).—By combining the formulæ of Ostwald-Poiseuille and of Scarpa (A., 1911, ii, 17), in which the density of the liquid does, and does not, occur respectively, it is possible to find the density by the viscosimeter. The results are in satisfactory agreement, and 2 c.c. or less of liquid are sufficient.

J. R. P.

**Determination of Density by means of the Pyknometer.**

WALTER BLOCK (*Zeitsch. angew. Chem.*, 1920, **33**, 198—200).—A discussion on the best way of using the pyknometer, attention being directed to sources of error in weighing, influence of atmospheric pressure, etc.

W. P. S.

**Internal Friction of Binary Mixtures of Liquids.**

JULIUS MEYER and BRUNO MYLIUS (*Zeitsch. physikal. Chem.*, 1920, **95**, 349—377).—The density and specific volume of benzene and fluoro-, chloro-, bromo-, and iodo-benzenes have been determined at tempera-

tures from  $0^{\circ}$  to the boiling point, and from calculations made from the Eötvös rule and the Trouton-Nernst formula it is shown that these substances are probably normal in the liquid condition. The density and specific volume of the binary mixtures of benzene and its halogen derivatives have been determined for various mixtures at temperatures between  $0^{\circ}$  and  $80^{\circ}$ . A comparison of the experimental specific volumes with those calculated by the mixture law from the individual specific volumes shows differences which lie within the experimental error, which indicate that the specific volume in these cases is an additive property. The viscosity-coefficient and fluidity of benzene and its monohalogen derivatives have been determined at temperatures between  $0^{\circ}$  and the boiling point. Below  $95^{\circ}$  fluorobenzene has a greater fluidity than benzene, despite its larger molecular weight. Above  $95^{\circ}$  the fluidity follows the expected order, that is, it is inversely proportional to the molecular weight. In all cases the  $v\phi$  curves are straight lines, and are in keeping with the Batschinski equation between  $v$  and  $\phi$  (A., 1913, ii, 928). The constants  $a$  and  $b$  of the Batschinski equation have been calculated for all five substances, and the observed and calculated values of  $\phi$  found to be extremely good. The fluidity of the binary mixtures mentioned above has been measured at temperatures  $0-80^{\circ}$ , and in these cases also the  $v\phi$  curves are straight lines. In general, the fluidity and internal friction cannot be calculated from any of the mixture formulæ hitherto applied. The formula  $\phi = \phi_1 \cdot b_1/b \cdot p_1(p_1 + p_2) + \phi_2 \cdot b_2/b \cdot p_2/p_1 + p_2$  has been deduced, which applies to all cases. J. F. S.

**Examination of Polányi's Theory of Adsorption.** LUDWIG BERÉNYI (*Zeitsch. physikal. Chem.*, 1920, **94**, 628-662. Compare A., 1916, ii, 474).—A theoretical paper in which a new method of calculating the partition of the adsorption potential in the adsorption space is developed. The method makes it possible to deduce this function from the isothermals of the adsorbed material above the critical temperature. This method has been applied to the adsorption isothermals of carbon dioxide, nitrogen, ethylene, carbon monoxide, methane, argon, and ammonia by charcoal, and sulphur dioxide and ammonia by silicic acid gels. The data used were obtained from the recent publications of Titoff (A., 1910, ii, 1041), Homfray (A., 1910, ii, 771, 1041), Richardson (A., 1917, ii, 526), and Patrick (Diss., Gottingen, 1914), and the results show that the demands of Polányi's hypothesis are moderately well fulfilled. The theory is applicable to the adsorption of vapours by silicic acid gels. J. F. S.

**Adsorption as a Molecular Phenomenon. I.** NIKOLAI SCHILOV and LIDIE LEPIN (*Zeitsch. physikal. Chem.*, 1920, **94**, 25-71).—The adsorption of a very large number of electrolytes and other substances from aqueous, alcohol, acetone, and toluene solutions by wood charcoal has been determined. The charcoal used was activated by treatment with superheated steam and purified

by treatment with hydrochloric acid (1:1). The experiments show that adsorption is due to the forces and properties of undissociated molecules. The adsorbent takes part in the process not only by means of its electro-capillary forces, but also by virtue of the whole of its molecular forces. Consequently, adsorption is not to be treated only as capillary chemistry, but also as molecular chemistry. The phenomena of adsorption show themselves to be the more or less complicated result of the molecular forces of the adsorbent, the adsorbed material, and the solvent. The adsorbent exercises a definite field of force, which is dependent on the chemical properties of all the substances concerned in the process, and thereby it becomes to a certain extent specific. For the production of an energetic power of adsorption two conditions are necessary; a difference in structure and definite chemical properties of the adsorbent or its impurities, whereby, however, a chemical reaction need not necessarily be brought about. The molecular field of force of the adsorbent depends on its composition. The adsorption of electrolytes containing either a common anion or cation exhibits characteristic regularities: (1) A series of electrolytes of different cations with the same anion when arranged in groups according to the valency of the cation shows the influence of the atomic weight of the cation and a relationship to its position in the periodic system, in the sense that the adsorption is greater the greater the atomic weight. A further series of the cations may be made with respect to hydrogen, in which those which are more electropositive fall into one group and those which are less electropositive fall into the other. (2) A series of electrolytes of various anions and one cation can be arranged into a number of groups of similar adsorptive properties; it is found that similar types of compounds occur in the same group. The following order of adsorption is found:  $\text{H}_3\text{XO}_3 \rightarrow \text{H}_3\text{XO}_4 \rightarrow \text{H}_2\text{XO}_4 \rightarrow \text{HXO}_3 \rightarrow \text{HXO}_4$ . The halogen and organic compounds may also be more or less regularly fitted into the complete series. In each group of a definite type the influence of the relative weight of the anion on the order of the adsorption is clearly marked in the sense that the greater the weight of the anion the more strongly is the substance adsorbed. The adsorption from a mixture of two substances is specific for each pair; it is not directly connected with the degree of dissociation, and cannot be completely explained by the mutual replacement of the substances by one another in the solid phase. The mutual influence of substances on their adsorption shows itself in the liquid phase in consequence of the change in the number of molecules in the solution, due to the formation of solvates or complex molecules. Two cases have been observed: (1) mutual increase in the adsorption of both substances; (2) change in the amount of adsorption of one substance in the presence of a second, which is practically not absorbed at all, for example, the action of neutral salts on the adsorption of acids, alkalis, and other salts with similar ions. The rôle of the solvent in the adsorption process shows itself not only in its own adsorption, but it is of a much

more important and general nature. The solvent, by virtue of its field of force, acts with the adsorbent in the partition of the adsorbed substance between the solid and liquid phases. This view is confirmed from the adsorption from mixed solvents. Here two types of curves and adsorption are observed, which show the dependence of the adsorption on the composition of the binary mixture of solvents: (1) the adsorption shows a definite minimum for a fixed composition of the solvent; (2) all mixtures of two solvents have an adsorption value which is the mean of that of the components.

The adsorption processes have a close connexion with the solubility phenomena, and with some of the facts of chemical kinetics, generally with all those processes in which the concentration of the undissociated molecule exerts itself and in which the influence of neutral salts has been observed. All such phenomena are to be regarded as due to molecular fields of force. J. F. S.

**Retention of Gases by Solid Substances. I. and II. Experiments on Carbonyl Chloride.** DOMENICO LO MONACO (*Arch. Farm. sper. Sci. aff.*, 1920, **29**, 3—47).—The preparation, properties, and uses of carbonyl chloride are described. The experiments made show that common materials, such as straw, hay, grass, soil, snow, fresh leaves, marine algæ, sawdust, charcoal and cotton, are capable, especially if moist, of absorbing to some extent the asphyxiating gases used in warfare. T. H. P.

**Adsorptive Stratification in Gels. IV.** SAMUEL CLEMENT BRADFORD (*Biochem. J.*, 1920, **14**, 474—482).—The formation of banded precipitates is due to adsorption of solute from the region between the bands. Only precipitates with great specific surface form bands. This factor is influenced by conditions, such as the reaction medium and the presence of ions. By varying its specific surface, a given substance may be obtained in a banded form or not, as desired; thus, by increasing the dispersity of silver chromate and dichromate, beautiful bands of both substances may be obtained in agar, a medium in which they do not usually form bands. J. C. D.

**Surface Tension of Vibrating Liquid Streams Investigated with Water and Aqueous Salt Solutions. H.** STOCKER (*Zeitsch. physikal. Chem.*, 1920, **94**, 149—180. Compare Pedersen, A., 1908, ii, 158).—The surface tension of water and of solutions of sodium, potassium, magnesium, calcium, copper, zinc and ferrous sulphates, sodium, potassium, ammonium, calcium, barium and magnesium chlorides, potassium bromide, nitrate, chlorate and perchlorate, sodium chlorate, mercuric cyanide, ammonia, and sucrose has been determined by measuring the amplitude of the wave produced when a stream of the solution emerges from an oval capillary tube under pressure. In the case of water at 18° the surface tension for the vibrating stream is found to be  $72.43 \pm 0.15$  dyne/cm., whilst the accepted value for stationary water is  $72.94 \pm 0.12$  dyne/cm. In the case of

all the solutions examined except that of ammonia, the surface tension under these conditions is found to be somewhat greater than, or in the limiting cases equal to, that of water at the same temperature.

J. F. S.

**Method of Determining Several Viscosities Simultaneously.** J. HOLKER (*J. Path. Bact.*, 1920, **23**, 177—184).—The method of Scarpa (A., 1911, ii, 17) has been modified, and a method devised for determining several viscosities simultaneously. The method depends on the measurement of two times,  $t_1$  and  $t_2$ , the former occupied in drawing up through a vertical capillary sufficient liquid to fill a bulb at the top of this tube, and the latter taken by the liquid in flowing out of the bulb under its own weight. Under constant conditions, the viscosity is then proportional to  $t_1 t_2 / (t_1 + t_2)$ .

J. R. P.

**Application of the Theory of Expansion Tension to the Study of Diffusion.** L. GAY (*J. Chim. physique*, 1920, **18**, 103—125).—A mathematical discussion of the subject.

W. G.

**Factors Affecting Rhythmic Precipitation.** ALFRED E. KOENIG (*J. Physical Chem.*, 1920, **24**, 466—477).—A number of experiments are described which show that the uniformity of the bands formed in rhythmic precipitation is uninfluenced by the structure of the gels. This non-uniform structure may be brought about by keeping the gel for some time before the solution is poured on it or by pouring the mixture of sodium silicate and acid just before it sets. The bands of the precipitate may be modified by the presence in the gel of substances such as alcohols, carbamide, and sucrose, all of which modify the rates of diffusion of the reacting substances and the solubility of the precipitated products. The rhythmic bands may be broken up more or less by the presence in the gel of various inert powders unevenly distributed and by the presence of small particles of soap, all of which tend to interfere with the uniform diffusion of the reacting substances. A series of experiments on the formation of rhythmic bands by the interaction in narrow tubes of such gases as ammonia with hydrogen chloride, bromide, or fluoride, and hydrogen sulphide with chlorine or sulphur dioxide has been described, and the relationship with similar reactions in gels pointed out. In addition to the effects of diffusion and the factors that modify it, there are also the effects of the concentrations necessary for precipitation to take place, the velocity of the reaction which forms the precipitate and the degree of supersaturation which the resulting substance may reach in a given medium, before precipitation takes place.

J. F. S.

**Diffusion and Mobility of Cobalt and Nickel Ions.** ELISABETH RONA (*Zeitsch. physikal. Chem.*, 1920, **95**, 62—65).—The diffusion constant,  $D$ , for cobalt chloride and nickel nitrate in aqueous and acid solutions has been determined by the method previously described (A., 1917, ii, 286), and the following values



obtained at 18°: cobalt chloride, in aqueous solution, 0.0127*N*,  $D=0.669$ ; in 0.1*N*-hydrochloric acid solution, 0.1*N*,  $D=0.634$ ; in 0.01*N*-hydrochloric acid solution, 0.01*N*,  $D=0.882$ ; nickel nitrate, in aqueous solution, 0.068*N*,  $D=0.802$ ; in 0.1*N*-nitric acid solution, 0.0413*N*,  $D=0.646$ ; in 0.01*N*-nitric acid solution, 0.0108*N*,  $D=0.719$ . In aqueous solution and in dilute acid solution the value of  $D$  decreases with decreasing salt concentration, but increases with decreasing concentration in the more concentrated acid solutions. As the solutions become more dilute the value of  $D$  approaches a limiting value which is the value of the bivalent ion. From these values, making use of the formulæ  $u=Dv/(0.0224v-D)$  and  $u=2D/0.0224$ , the mobility of the bivalent ions has been calculated and the values  $Ni=48.0$  and  $Co=47.7$  obtained. J. F. S.

**Diffusion Experiments with Highly Active Saccharase Preparations.** H. VON EULER, A. HEDELIUS, and O. SVANBERG (*Zeitsch. physiol. Chem.*, 1920, **110**, 190—216).—Diffusion experiments with different saccharase preparations have given velocities of diffusion of varying magnitudes, and consequently the calculated molecular weights also showed significant variations. The authors conclude that the substrate and the products of the enzymic action do not diminish the size of the colloidal particles of the saccharase, and the velocity of diffusion at the optimum acidity required for the action of the enzyme is not essentially different from that in water. S. S. Z.

**Permeability of Thin Fabrics and Films to Hydrogen and Helium.** J. C. McLENNAN and W. W. SHAVER (*Phil. Mag.*, 1920, [vi], **40**, 272—280; see Elworthy and Murray, this vol., ii, 508).—The rate of diffusion of hydrogen through a series of balloon fabrics has been determined. The permeability of soap films of thickness corresponding with the reddish-green stage is, for helium, 670 litres per sq. m. per day, and for hydrogen 960 litres per sq. m. per day, at 20°. The rate of transfusion of helium through soap films is 0.70 times that for hydrogen through similar films. The diffusion of hydrogen through water films filling the interstices of wet cotton fabric is very low. J. R. P.

**Anomalous Osmosis of some Solutions of Electrolytes with Gold-beater's Skin Membranes.** F. E. BARTELL and O. E. MADISON (*J. Physical Chem.*, 1920, **24**, 444—465).—The osmotic effects of a number of solutions with gold-beater's skin have been examined with the object of ascertaining whether any parallelism exists between the observed effects and the potential difference associated with the same combination. In the case of sucrose it is shown that the rate of osmosis is very nearly proportional to the concentration of the solution. The direction and the magnitude of the flow of solution are, in practically every case, exactly those which would be predicted. If the solution side of the membrane

is of the same electrical sign as the capillary liquid layer the resulting osmosis will be abnormally low or negative, whereas if these parts of the system are of opposite sign the resulting osmosis will be abnormally high. With salts of univalent and bivalent cations the superimposed effect is found to work in opposition to the normal osmosis, with the result that the observed rate of osmosis is less than normal. With salts of aluminium and thorium the superimposed effect works in conjunction with the normal osmosis, and the result is an abnormally large osmosis. Increase in concentration causes but slight increase in the osmosis of solutions of univalent cations, a marked decrease in the osmosis of solutions of bivalent cations and a decidedly greater increase in the osmosis of solutions of trivalent and quadrivalent cations. A logical explanation of the facts seems to be that with dilute solutions of univalent and bivalent cations, the charges of the membrane against the solution is at all times electronegative, which tends to produce an abnormally low osmosis. In the case of solutions of bivalent cations there is a marked tendency to neutralise the negative charge of the membrane, with the result that with more concentrated solutions the membrane approaches the isoelectric point and osmosis now approaches the normal rate. In the case of solutions of trivalent and quadrivalent cations, the sign of the membrane is positive, even with very dilute solutions; this results in an abnormally large positive endosmosis in every case. With two-compartment cells, the concentrations of the solutions on the two sides of the membrane are much more nearly equal than in the one-compartment cell. This is due to the small initial water volume, with the result that the *E.M.F.* of the membrane system is, in this case, much less than in the case of the one-compartment cell. Owing to the smaller potential difference between the two faces of the membrane, the resulting osmosis is in all cases more nearly normal. In the case of solutions of univalent cations, there exists a smaller tendency to negative osmosis, whereas in the case of solutions of multivalent cations, such as thorium and aluminium, there exists a smaller tendency for an abnormally great positive osmosis. In the case of dilute acid the tendency is toward an abnormally great positive osmosis. As the concentration of the acid is increased, the sign of the capillary system is reversed, and the osmotic tendency passes from abnormally great positive to normal, and then to abnormally small, and finally to negative osmosis. In the case of sodium hydroxide a negative tendency persists throughout. At the higher concentrations the electrical factors of the system are such that negative osmosis results. Porcelain membranes yield similar results with acids and alkalis.

J. F. S.

**Thermodynamics of Mixtures. I.** MARIO BASTO WAGNER (*Zeitsch. physikal. Chem.*, 1920, **94**, 592—627).—A mathematical paper in which the equilibrium and reversibility conditions are deduced for purely physical and physico-chemical mixtures.

J. F. S.

**Thermodynamics of Mixtures. II. and III.** MARIO BASTO WAGNER (*Zeitsch. physikal. Chem.*, 1920, **95**, 15—36, 37—61. Compare preceding abstract).—A mathematical paper in which expressions are developed in connexion with the osmotic pressure of solutions of any concentration. The volume of mixtures is considered as a function of the volumes of the components and the heat of mixture. Four methods of calculating the degree of association of anomalous substances are deduced, and expressions for calculating the heat of mixing are developed. J. F. S.

**The Solubility of Acraldehyde in Water and of Water in Acraldehyde at Different Temperatures.** A. BOUTARIC (*J. Chim. Phys.*, 1920, **18**, 126—132).—The author has measured the solubilities of water in acraldehyde and of acraldehyde in water over the temperature range  $-10^{\circ}$  to  $+50^{\circ}$ . The presence in acraldehyde of such substances as quinol or gallic acid, used to stabilise it, causes a diminution in the solubility of acraldehyde in water and an increase in the solubility of water in acraldehyde. W. G.

**Ionic Radius and Ionic Efficiency.** JACQUES LOEB (*J. gen. Physiol.*, 1920, **2**, 673—687).—It has been shown previously that when solutions of electrolytes are separated from pure water by collodion membranes, the ions with the same sign of charge as the membrane increase, whilst the ions with the opposite sign of charge diminish, the rate of diffusion of water from the side of pure water to the side of solution, and that the accelerating and depressing effects of these ions on the rate of diffusion of water increase with their valency. It is now found that, aside from the valency, a second quantity of the ion plays a rôle in this effect, namely, the radius, which in a monatomic ion means the distance between the central positive nucleus and the outermost ring or shell of electrons of the ion. In monatomic, univalent anions the radius increases in the order  $\text{Cl} < \text{Br} < \text{I}$  (being largest in I), whilst for monatomic, univalent cations it increases in the order  $\text{Li} < \text{Na} < \text{K} < \text{Rb}$  (being largest in Rb). The accelerating as well as the depressing effect of the anions mentioned increases directly with the order of magnitude of their radius, and the efficiency is greatest in the case of iodine, which has the largest radius; the accelerating as well as the depressing effect of the cations increases inversely with the order of magnitude of their radius, lithium with the smallest radius having the greatest efficiency. This is intelligible on the assumption that the action of the ions is electrostatic in character, in the case of cations due to the electrostatic effect of the excess charge of their positive nucleus, and in the case of anions due to the excess charge of their captured electron. The electrostatic effect of the positive nucleus of a cation on the membrane (or any other body) will be the greater the smaller the ionic radius of the cation; and the electrostatic effect of an excess electron will be the greater the further its distance from its own positive nucleus. It is suggested that this rule

may possibly include polyatomic, univalent ions (such as  $\text{NO}_3$ ,  $\text{CNS}$ , etc.) if these are replaced by monatomic models in which the radius is calculated in such a manner as to give the model the same electrostatic effect which the polyatomic ion possesses. These conclusions are in harmony with the fact that the efficiency of ions increases also with their valency. It is suggested that these rules concerning the influence of the ionic radius can possibly be demonstrated in other phenomena, depending on the electrostatic effect of ions.

H. W.

**Relationship between the Non-dissociated Part  $(1 - \alpha)$  of Dissolved Salts and the Dielectric Constant  $\epsilon$  of the Solvent.**

P. WALDEN (*Zeitsch. physikal. Chem.*, 1920, **94**, 374—404).—From a consideration of a large amount of experimental data it is shown that for a salt in a given solvent the product  $(1 - \alpha) \sqrt[3]{v}$  is constant over a wide range of dilution, that is,  $(1 - \alpha) \sqrt[3]{v} = \text{const.}$ , or  $(1 - \alpha) = \text{const.} / \sqrt[3]{v} = \text{const.} \cdot c^{\frac{1}{3}}$ . The undissociated portion of the electrolyte  $(1 - \alpha)$  is therefore directly proportional to the linear concentration  $c^{\frac{1}{3}}$ , or the distance between the molecules in the solution. The constant  $(1 - \alpha) \sqrt[3]{v} = K$  is practically the same for different typical binary salts in every solvent, provided that the electrolytes are about equally strong in aqueous solution; this constant is characteristic for the binary salts examined, and fluctuates only slightly about a mean value. When the dielectric constant is taken into account, a constant value is obtained which is fundamental to the above-mentioned constant, and this applies to solvents of the most widely differing character; this constant is represented by  $(1 - \alpha) \cdot \epsilon \cdot \sqrt[3]{v} \sim \text{const.} \sim 41.5$ , or  $(1 - \alpha) \sim \text{const.} \cdot c^{\frac{1}{3}} / \epsilon$ , that is, in different solvents the undissociated portion of the electrolyte is almost directly proportional to the linear concentration,  $c^{\frac{1}{3}}$ , and indirectly proportional to the dielectric constant,  $\epsilon$ , of the solvent.

J. F. S.

**Some Thermodynamical Formulæ.** RUDOLF WEGSCHEIDER (*Zeitsch. physikal. Chem.*, 1920, **94**, 739—762).—A mathematical

paper in which it is shown that the van't Hoff reaction isothermal, which is based on the well-known osmotic pressure equation, for dilute solutions assumes in its deduction that for changing concentration the total pressure changes in such a way that the partial pressure of the solvent remains constant. Consequently, the isothermal does not refer strictly to constant volume relationships. This reaction isotherm, from its kinetic derivation, appears to be applicable for constant volume relations, but strictly it is for this purpose only an approximation formula. The strictly developed reaction isotherm of Planck, which is based on the additivity of the volume and internal energy of dilute solutions, is different from that of van't Hoff, and leads to a different law for osmotic pressure, which agrees better with experimental observations than that of van't Hoff, and therefore is to be preferred. There is practically an objection to this formula, for it

contains the molecular fraction, and in the case of associated solvents, for example, water, the fraction is not accurately known. The Helmholtz equation,  $T(d\Delta A/dT)_v = \Delta U + \Delta A$ , is true, not only for constant volume, but also when isothermal processes at various temperatures are carried out in such a way that the change in volume remains the same. If the same isothermal process at different temperatures is carried out in such a way that the change in pressure remains exactly the same, the formula  $(d\Delta A/dT)_p = d\Delta p v/dt + (\Delta U + \Delta A)/T$  holds. For complete equilibrium, these formulæ are not applicable. In this case, the equation  $d\Delta A/dT = p d\Delta v/dT + (\Delta U + \Delta A)/T$  is applicable. On the basis of the Nernst theorem, a vapour-pressure formula is deduced in which the only approximation made is that the vapour is treated as an ideal gas. On the basis of this formula, equations are developed for the equilibrium constants in gas reactions and for the dependence of the heat of vaporisation on the temperature. J. F. S.

**Relationship between the Electrolytic Dissociation and the Dielectric Constant of Solvents.** P. WALDEN (*Zeitsch. physikal. Chem.*, 1920, **94**, 263—294).—Making use of ionisation data previously obtained by the author (A., 1906, ii, 149) and by other investigators, by means of which it was shown that  $\epsilon^3\sqrt{v} = \text{constant}$ , it is now shown that all these practically equally strong salts in many solvents at the same dissociation step  $\alpha' = \alpha'' = \text{const.}$ , and the corresponding dilution,  $v$ , completely fulfil the equation  $\epsilon = \sqrt[3]{v} = \text{const.}$  The degree of dissociation has the value  $\alpha' = 0.50$ ,  $\alpha'' = 0.666$ , and in the third case,  $\alpha''' = 0.86$ , the dilution varied; for example, with constant degree of dissociation  $\alpha''' = 0.86$ ,  $v$  varied between 16 and 8000 litres. The Ostwald constant,

$$K_0 = \alpha^2/(1-\alpha)v,$$

has been calculated for the same degree of dissociation in all solvents; by combining these two equations, the expression  $\epsilon/\sqrt[3]{K_0} = \text{constant}$  is found for a given  $\alpha$  value in all solvents, or the Ostwald constant,  $K_0 = \epsilon^3 \cdot \text{const.}$ , where  $\epsilon$  is the dielectric constant of the solvent. For infinite dilution,  $v = \alpha$ .  $\alpha = 1.00$  const., and  $K_0 = (0.0054\epsilon)^3$ . The dissociation constant for the typical strong binary salts in any solvent can be calculated by means of the equation for the condition when  $\alpha = 1.0$ . The values thus obtained agree in many cases exactly, and in others very nearly, with the experimentally determined values. For one and the same salt, tetrapropylammonium iodide, the value of  $K_0$  varies from 0.14 in formamide and hydrogen cyanide to 0.0000017 in benzene and carbon tetrachloride, or approximately in the ratio 100000:1. The cause of the decrease in the Ostwald constant with increasing dissociation is probably to be found in the fact that in a given solvent this deviation from the law of mass action is approximately proportional to the concentration of the undissociated salt, that is, for different  $\alpha$ -values,

$$K_0' : K_0'' : : (1-\alpha') : (1-\alpha''),$$

or  $K_0/(1-\alpha) = \text{const.} = K_1$ . Transforming this to different solvents,  $\epsilon/\sqrt[3]{K_1} \sim \text{const.} \sim 78$ .

J. F. S.

**Molecular Condition of Binary Salts in Weakly Ionising Solvents. Solvation and Polymerism.** P. WALDEN (*Zeitsch. physikal. Chem.*, 1920, **94**, 295—373).—The author has examined the condition of binary salts in weakly ionising solvents by means of data previously published by the author himself and others, and also certain other fresh data now published. It is shown that solvolytic dissociation, as well as polymerisation of the dissolved molecules, are common phenomena in non-aqueous solutions. Both phenomena occur simultaneously, particularly in solvents with small dielectric constants, or one and the same solvent can promote a far-reaching solvolysis and a high degree of polymerisation. Acetic acid is a solvent which favours polymerisation. The highest degree of solvolysis is found in media which are practically insulators, such as naphthalene, benzene, carbon disulphide, and chlorinated hydrocarbons, and consequently the solvolytic dissociation cannot depend on ion formation or ion action. The degree of solvolysis of different salts of a common acid is influenced by (a) the strength of the base in the salt, and (b) the affinity of the medium towards one component of the salt, that is, the power of the solvent to form molecular compounds with the acid or base of the salt. One and the same salt can, according to the solvent, show all possible degrees of polymerisation; the degree of association,  $x$ , of its molecules can vary between  $x = \infty$  and  $x \leq 1$ , and here the dielectric constant of the solvent,  $E$ , plays the determining rôle; the degree of association is greater the smaller the value of  $E$ . Quantitatively, it is found for similar degrees of association  $x_1 = x_2 = \text{constant}$  in various solvents the dielectric constants of which are  $E_1, E_2, E_3$ , and the corresponding dilutions  $v_1, v_2, v_3$ , that the expression  $E_1 \sqrt[3]{v_1} = E_2 \sqrt[3]{v_2} = \text{constant}$ , holds. When this expression is re-formed for different degrees of association, the general approximate expression  $x \cdot E \sqrt[3]{v} \sim \text{const} \sim 36$  is obtained. Since these relationships between the degree of depolymerisation of salt molecules and the dielectric constant,  $E$ , of the solvent are exactly the same as those between the electrolytic dissociation of the same salt molecules in ionising solvents, it follows that it is likely that depolymerisation occurs according to the scheme

$$(\text{MeX})_2 \rightleftharpoons \text{MeX}^+ + \text{MeX}^-$$

J. F. S.

**Structure of Precipitates.** SVEN ODÉN (*Svensk. Kem. Tidskr.*, 1920, **5**, 74—85; from *Chem. Zentr.*, 1920, iii, 223).—The author has drawn conclusions as to the structure of precipitates from microscopical investigation and determination of the velocity of sedimentation by the continuous weighing of the sediment falling on a metal plate placed at the bottom of the solution. From sufficiently supersaturated solution, primary particles of the magnitude  $1 \mu\mu$ — $10 \mu$  are initially formed, which only remain unchanged in exceptional cases. In general, secondary aggregates are further formed, which sink rapidly; these aggregates can frequently be disintegrated by agitation. The author develops

the relationship between the amount of precipitate which has fallen to the bottom and the time by a series of graphs (accumulation graphs), and distinguishes types of reversible and irreversible aggregation. The irreversible aggregates grow continuously, whilst the reversible ones attain a maximal magnitude for which an aggregation period can be found. The influence of the concentration of the electrolyte on the time of aggregation is in harmony with the investigation of Westgren (this vol., ii, 99). The alteration in the time of aggregation with the number of particles was investigated for a constant electrolyte content at the instance of the precipitation of barium sulphate in the presence of citric acid as coagulator, and the results are in agreement with von Smoluchowski's coagulation formula (A., 1917, ii, 297). The cause of the formation of secondary aggregates lies in capillary and adhesion forces, which bring about the coagulation of the colloidal particles. The size of the aggregates increases as the difference in potential between the particles and the liquid diminishes. It has been found possible, under perfectly definite conditions, to calculate the number of primary particles in an aggregate for a suspension of barium sulphate with citric acid as electrolyte. Aggregation and disaggregation have been investigated with increasing additions of this electrolyte.

H. W.

**Retardation of Crystallisation in Supersaturated Solutions.** ERNST COHEN and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1920, **94**, 482—504).—The relationship of the solubility of cadmium iodide to pressure has been examined at 30°, and the relationship between the volume and concentration found to be given by the expression  $v_c = 1.00435 - 0.820924c + 0.016857c^2$ . The crystallisation of saturated solutions has also been studied, and it is shown that strongly supersaturated solutions may, even in the presence of the solid phase, be caused to crystallise very slowly, in consequence of the presence of small quantities of a third substance. The saturation concentration may apparently, and very slowly, be overstepped at a given concentration in the presence of a small quantity of a third substance.

J. F. S.

**Symmetry of the Röntgen Patterns obtained by means of Systems Composed of Crystalline Lamellæ, and the Structure of Pseudo-symmetrical Crystals.** F. M. JÄGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 815—830).—Röntgen patterns have been obtained by passing the rays through plates of muscovite (0.32 mm. thick) which crossed one another at various angles (45° or 60°). The patterns obtained indicate that if the central part of a regular complex of crystalline lamellæ, cut perpendicular to a plane of symmetry of the crystals, and crossing at angles  $\alpha = 2\pi/n$ , be radiated by Röntgen rays, the normal diffraction pattern thus obtained will exhibit an axis of  $n$ -fold symmetry, showing, therefore, the image of the original pattern repeated  $n$  times. The diffraction image of the dextro-

and lævo-rotatory complexes of this kind are always identical. Reproductions of photographs of the patterns obtained are given in the paper.

J. F. S.

### **Bragg's Work and the Law of Definite Proportions.**

A. QUARTAROLI (*Gazzetta*, 1920, **50**, ii, 60—64).—From the investigations of Bragg on crystals of sodium chloride and analogous compounds, diamond, pyrites, etc., it follows that such crystals represent a homogeneous mixture of atoms distributed regularly in space. For instance, in the case of iron pyrites, the elementary cube has four atoms of iron at alternate corners and an atom of sulphur in the interior. An aggregation of  $n^3$  such cubes has the composition  $\text{Fe}_{(n+1)^3}\text{S}_{2n^3}$ , which approximates to  $\text{FeS}_2$  when  $n$  is very large, but when  $n$  is 50 and the aggregate of the order of magnitude of granules visible by the ultramicroscope, the composition is represented by the formula  $\text{FeS}_{1.885}$ . It is therefore possible that continuous variations may occur in the chemical composition of micro-crystals in accordance with the magnitude of such crystals when deposited; with pyrites, the composition might vary from  $\text{Fe}_4\text{S}$  to  $\text{FeS}_2$ .

T. H. P.

### **The Reversal of the Sign of the Charge of Collodion Membranes by Tervalent Cations.**

JACQUES LOEB (*J. gen. Physiol.*, 1920, **2**, 659—671).—Tervalent cations cause a collodion membrane covered with a protein film to be charged positively, whilst they do not produce such an effect on collodion membranes not possessing a protein film. The same has been found for the reversal of the sign of charge of the membrane by acid. This reversal in the sign of charge of the membrane by tervalent cations occurs on the alkaline side of the isoelectric point of the protein used, whilst the reversal by acid occurs on the acid side of the isoelectric point. The reversal seems to be due to, or to be accompanied in both cases by, a chemical change in the protein. The chemical change which occurs when the hydrogen ions reverse the sign of charge of the protein film consists in the formation of a protein-acid salt, whereby the hydrogen ion becomes part of a complex protein cation, whilst the change which takes place when tervalent cations reverse the sign of charge of the protein film consists in the formation of an insoluble, and therefore sparingly or non-ionisable, metal proteinate.

H. W.

### **A Series of Abnormal Liesegang Stratifications.**

EMIL HATSCHKE (*Biochem. J.*, 1920, **14**, 418—421).—A number of such abnormalities, which were encountered when attempts to obtain stratification of calcium phosphate in gelatin were made, are described and illustrated. It is obviously impossible to attempt an explanation of these abnormal results in the present unsatisfactory state of knowledge regarding the normal phenomenon.

J. C. D.

### **Application of Smoluchowski's Equation to the Change with Time of the Number of Particles in an Emulsion.**

P. C. VON ARKEL (*Physikal. Zeitsch.*, 1920, **21**, 465—467).—Accord-



ing to Smoluchowski (see A., 1916, ii, 302), the formula deduced by him for the Brownian movement is in agreement with the observations of Svedberg ("Existenz der Moleküle," 1912, p. 148). It is shown that this agreement is not sufficiently close when all the deductions of Smoluchowski are compared with the experimental numbers. The differences are probably to be explained by the incompleteness of the series of observations rather than by defects in the theory.

J. R. P.

**Conductivity Depression and Adsorption by Lyophile Colloids.** M. POLÁNYI (*Biochem. Zeitsch.*, 1920, 104, 237—253).

—The name "*L*-effect" is given to the percentage by which the electrical conductivity of a mixture of electrolyte and colloidal solution falls short of that of the colloid-free disperse medium of the same mixture; the specific *L*-effect refers to 1 gram of dissolved colloid. Whereas crystalloids lower the conductivity in the same measure as they raise the viscosity of the solvent, colloids depress the conductivity far less than the fluidity; this discrepancy indicates that the ions in colloidal solutions set in motion only the disperse medium, and not, to any extent, the colloidal particles.

The method employed to measure the *L*-effect consists in leaving a parchment thimble containing a colloidal solution immersed in a definite quantity of water until the diffusion reaches a condition of equilibrium, and then measuring the electrical conductivities of the colloidal solution remaining inside the thimble and of the pure, disperse medium from the outer vessel. The results thus obtained with various colloids and electrolytes are given, and calculations made of the "non-conducting space," that is, the volume per gram of colloid calculated on the assumption that the colloidal particles, by their mere presence, diminish the number of ions per c.c. and prolong their paths. This assumption almost suffices to account for the magnitudes found for the *L*-volume.

The swelling of colloidal substances indicates that part of the disperse medium is held by the colloidal particles, and the assumption may be made that the small amounts by which the non-conducting space exceeds the specific volume of colloidal substances, namely, 0.8, have their origin in the increase in size of the colloidal particles caused by the aqueous envelope. Explanations of the depression of the conductivity of electrolytes by colloids other than the purely mechanical one appear to be excluded by the following observations: (1) The *L*-effect of casein is the same when the casein is dissolved as sodium caseinate as when it is simply suspended in the coarsely granular, undissolved condition. (2) The *L*-effect is, within wide limits, proportional to the concentration of the colloid. This hypothesis assumes that all the ions in an electrolyte are influenced to the same extent by a colloid, but since Cybulski and Dunin-Borkowski (*Krak. Anz.*, 1909, 660) have found that the transport numbers are altered considerably by the presence of colloids, the author makes the further assumption that the aqueous envelopes of the colloidal particles are permeable to varying degrees

for different ions; this assumption also serves to explain the effect of the colloid on the diffusion potential.

The adsorption of electrolytes in colloidal solution is also considered, use being made of the equilibrium dialysis to determine the "non-dissolving space," that is, the space taken up by the colloid. If the specific volume of the colloid is 0.8, positive or negative adsorption is shown by the non-dissolving space per gram of colloidal substance being smaller or larger than 0.8. It has been shown thermodynamically that substances which increase (or diminish) the osmotic pressure of colloids are adsorbed positively (or negatively) (A., 1914, ii, 720). Since continued diminution of the osmotic pressure must lead finally to coagulation, the obvious conclusion is that coagulating substances must be negatively, and those which hinder coagulation positively, adsorbed. This conclusion requires experimental proof, but is supported by the fact that dextrose, which retards the coagulation of albumin considerably, is positively adsorbed by albumin to a marked extent.

T. H. P.

**Undamped Oscillations derived from the Law of Mass Action.** ALFRED J. LOTKA (*J. Amer. Chem. Soc.*, 1920, **42**, 1595—1599).—A theoretical paper in which it is shown that in certain circumstances conditions may be obtained in an homogeneous system for the production of undamped oscillations in the absence of any geometrical cause.

J. F. S.

**Statistical Meaning of the Thermodynamical Functions.** KARL F. HERZFELD (*Zeitsch. physikal. Chem.*, 1920, **95**, 139—153).—A mathematical paper in which a number of statistical formulæ are discussed and the difference between the external work and the added heat pointed out. The dependence of the total energy on the temperature is discussed. Using the same formulæ, the conditions of chemical equilibria and chemical potential for gaseous and dilute solution systems are developed. The equations deduced in the last cases are then applied to the formulæ of von Laues.

J. F. S.

**Temperature-coefficients of the Action of Saccharase.** HANS VON EULER and INGVAR LAURIN (*Zeitsch. physiol. Chem.*, 1920, **110**, 55—92).—Determination of the velocities of inversion by saccharase at pairs of different temperatures shows that the constant  $A$  of Arrhenius's temperature formula (this vol., i, 506) varies with the temperature in accordance with the equation  $A = 11,400(1 - 0.009t)$ , which is in agreement with the results of Kjeldahl (A., 1883, 225) and O'Sullivan and Thompson (T., 1890, 57, 834).

There is no theoretical basis indicating the independence of the constant  $A$  on the temperature; according to Arrhenius (A., 1889, 1103),  $A$  represents the heat change of the reaction, and there is no reason to assume that this heat change must always be independent of the temperature. On the other hand, the

Arrhenius temperature formula agrees well with the experimental results over a wide range of temperature, especially for the inversion of sucrose by acids. On the assumption that the velocity of the enzymic inversion of sucrose is proportional to the concentration of the complex molecule, sucrose-enzyme, the temperature-coefficient of the inversion is determined by the following magnitudes: (1) the influence of the temperature on the concentration of the active enzyme; (2) the influence of the temperature on the reactivity of the compound, sucrose-enzyme (and the reactivity of the water); and (3) the alteration of the equilibrium, sucrose: enzyme, with temperature. The last of these may be determined quantitatively on the basis of Michaelis and Menten's theory (A., 1913, i, 540), according to which  $[S][E - \phi] = K[\phi]$ , where  $[S]$  is the concentration of the free substrate,  $[E]$  the total molar concentration of the enzyme,  $[\phi]$  the concentration of the combined enzyme or of the compound, sucrose-enzyme, and  $K_M$  the equilibrium constant. The value of the velocity of inversion is given by  $v = C[\phi] = C[E][S]/([S] + K_M)$ ,  $C$  being a proportionality factor; influence (2) is expressed in the factor  $C$  and influence (3) in  $K_M$ .

The authors have measured the values of the constant  $K_M$  of the equilibrium between sucrose and enzyme for the temperature interval 0—40°, use being made of methods essentially the same as that of Michaelis and Menten (*loc. cit.*). At 25° and for the optimal acidity ( $p_H = 4.5$ ), the value of  $K_M$  is found to be  $26.10^{-3}$ , which remains unchanged over the acidity region  $p_H = 3.35-5.65$ ; the above authors gave  $16.10^{-3}$ . Three-fold increase of the concentration of the enzyme is without influence on the value of  $K_M$ .

The equilibrium constants of the equilibrium  $[S][E - \phi] = K_M\phi$ , obtained for the temperatures 1°, 15°, 25°, and 39°, show that the equilibrium is altered approximately by 1% per degree rise of temperature; the values obtained at these temperatures agree well with those calculated with the help of the heat of dissociation,  $Q$ , this being found by the equation  $Q = -RT^2 \cdot d \log k / dT = -[4.58(\log K_2 - \log K_1)T_1T_2]/(T_2 - T_1)$  to have the mean value 2000 cal.

As regards the great difference between the temperature-coefficients for enzymic inversion (9400 at 20°) and acid inversion (25,600 at 20°), the results obtained show that this is not due to abnormal alteration of the equilibrium enzyme:sucrose, but that it can depend only on increase in concentration of the compound, sucrose-acid, as the temperature rises.

T. H. P.

**Ester Formation in Absolute Ethyl Alcohol.** HEINRICH GOLDSCHMIDT, J. ANDERSON, M. FEIGL, G. GÖRBITZ, J. SCHJERVE, L. SVENDSEN, A. THUESEN, O. UDBY, and P. WRÅA (*Zeitsch. physikal. Chem.*, 1920, **94**, 233—253).—The rate of esterification of acetic acid in absolute alcohol has been determined with trichlorobutyric, trichloroacetic, picric, hydrochloric, and sulphosalicylic acids as catalysts. Similar experiments with the same

catalysts have been carried out for the rate of esterification of propionic, *n*-butyric, *isobutyric*, *n*-valeric, *isovaleric*, pivalic, heptioic, phenylacetic, phenylpropionic, and glycollic acids. The results in all cases show that the rate of esterification is satisfactorily represented by the formula  $k = c[K_A\gamma + K_B(1 - \gamma)]$ . The results also show that both the ions and the undissociated acid act catalytically. The velocity-constant for the undissociated portion of the catalyst,  $K_B$ , is in general the greater the greater the affinity-constant of the catalyst. The relationship of  $K_A$ , the velocity-constant of the reaction catalysed by the hydrogen ions, to  $K_B$  is in general, for the different acids with one and the same catalyst, not constant. The relationship  $K_A/K_B$  in the case of hydrochloric acid as catalyst is not equal to unity, but considerably greater, in all cases investigated. For calculating the present results, the degree of dissociation of picric acid was necessary. This has been obtained from electro-conductivity determinations of aniline picrate in alcohol solution. The value  $\lambda_\infty = 49$  is obtained. The values of  $K_A$  and  $K_B$  are given for all cases examined. J. F. S.

**Formation and Hydrolysis of Lactones.** A. KAILAN (*Zeitsch. physikal. Chem.*, 1920, **94**, 111—128).—A theoretical paper in which the experimental results of P. Henry (A., 1892, ii, 1303) on the rate of formation of the lactones of  $\gamma$ -hydroxybutyric acid and  $\gamma$ -hydroxyvaleric acid have been recalculated. It is shown that, in the above-named reactions in aqueous solution with strong acids as catalysts, the catalytic action of the undissociated acid, if it is present at all, is in any case much smaller than that of the hydrogen ion. The velocity-coefficients have been calculated for the experiments of Johansson and Sebelius (A., 1918, ii, 223) on the hydrolysis of  $\gamma$ -butyrolactone and  $\gamma$ -valerolactone with nitric acid as catalyst, and it is shown that here also the velocity of the reaction is proportional to the concentration of the hydrogen ion rather than to that of the total acid. The demands of the theory, that, starting from either the hydroxyacids or the lactones, the same value must be obtained for the sum of the constants of the velocity of hydrolysis or lactone formation, are fulfilled within the possible experimental error. The apparent contradiction, furnished by Henry's results on lactone formation with acetic acid as catalyst and also without catalyst, to the hypothesis of a pure hydrogen-ion catalysis can be, to a large extent, brought into line with this hypothesis by the assumption that most of the products used by Henry contained small amounts of silver salts from their preparation. This leaves out of consideration the action of the undissociated molecule, if such exists. J. F. S.

**Quantitative Kinetic Analysis in the Case of Bimolecular Reactions.** L. SMITH (*Zeitsch. physikal. Chem.*, 1920, **95**, 66—94).—The kinetics of reactions of mixtures are discussed theoretically with the object of deducing methods by which the composition of a mixture of two allied and difficultly separable substances may

be ascertained from the velocity-constant of a reaction carried out with the mixture and a given reagent, such as the rate of hydrolysis of a mixture of esters with alkali hydroxide. Two methods are elaborated, the first, a graphic method which is applicable when the reaction-constants of the pure components, as well as that of the mixture, are all known, and the second, a mathematical method applicable when the reaction-constants for the mixture and one component are known, and when one of the components reacts much more rapidly than the other. The methods are applied to the reaction of barium hydroxide on mixtures of  $\alpha$ - and  $\beta$ -glyceryl chlorohydrin and to the hydrolysis of a mixture of ethyl butyrate and acetate by the same reagent. The results show the value and trustworthy character of both methods. J. F. S.

**Ageing of Colloidal Catalysts (Platinum, Palladium).** GREGORIO DE ROCASOLANO (*Compt. rend.*, 1920, 171, 301—303).—The catalytic activity of electrosols of platinum and hydrosols of palladium increases at first with age until it reaches a maximum, and then decreases. W. G.

**Influence of the Substrate Concentration on the Rate of Hydrolysis of Proteins by Pepsin.** JOHN H. NORTHRUP (*J. gen. Physiol.*, 1920, 2, 595—611).—It is pointed out that the apparent exceptions to the law of mass action found in enzyme reactions are also encountered in catalytic actions in strictly homogeneous solutions. These deviations may be explained by the hypothesis that the active mass of the reacting substances is not directly proportional to the total concentration of substance taken. In support of this suggestion, it is shown that for any given concentration of pepsin the relative rate of digestion of concentrated and of dilute protein solutions is always the same. If the rate of digestion depended on the saturation of the surface of the enzyme by substrate, the relative rate of digestion of concentrated protein solutions should increase more rapidly with the concentration of enzyme than that of dilute solutions. This is found not to be true, even when the enzyme could not be considered saturated in the dilute protein solutions.

The rate of digestion and the conductivity of egg-albumin solutions of different concentration are found to be approximately proportional at the same  $P_H$ . This agrees with the hypothesis first expressed by Pauli, that the ionised protein is largely or entirely the form which is attacked by the enzyme. The rate of digestion is diminished by a very large increase in the viscosity of the protein solution; this effect is probably mechanical in nature and due to the retardation of the diffusion of the enzyme. H. W.

**Catalysis with Platinum Black. II.** E. OLIVERI-MANDALÀ (*Gazzetta*, 1920, 50, ii, 81—89. Compare A., 1916, ii, 615).—According to Traube's hypothesis, the function of platinum black in the catalysis of hydrogen peroxide is represented by the equa-

tions:  $n\text{Pt} + y\text{H}_2\text{O}_2 = \text{Pt}_n\text{O}_y + y\text{H}_2\text{O}$  and  $\text{Pt}_n\text{O}_y + y\text{H}_2\text{O}_2 = n\text{Pt} + y\text{H}_2\text{O} + y\text{O}_2$ . This hypothesis scarcely seems capable of extension to the catalyses of ammonium nitrite, azoimide, hydroxylamine, and hydrazine, represented by the respective equations  $\text{NH}_4\text{NO}_2 = 2\text{H}_2\text{O} + \text{N}_2$ ,  $3\text{N}_3\text{H} = 4\text{N}_2 + \text{NH}_3$ ,  $4\text{NH}_3\text{O} = 2\text{NH}_3 + \text{N}_2\text{O} + 3\text{H}_2\text{O}$ , and  $2\text{N}_2\text{H}_4 = 2\text{NH}_3 + \text{N}_2 + \text{H}_2$ , especially when the absence of oxygen from azoimide and hydrazine is considered. It may be that the catalyst reacts with water, forming a platinum oxide and hydrogen, catalytic oxidations and reductions being thus rendered possible. In this way, it is possible to explain the different steps in the three different catalytic decompositions of hydrazine, namely, (1)  $2\text{N}_2\text{H}_4 = 2\text{NH}_3 + \text{H}_2 + \text{N}_2$ , (2)  $3\text{N}_2\text{H}_4 = \text{N}_2 + 4\text{NH}_3$ , and (3)  $3\text{N}_2\text{H}_4 = 2\text{N}_2 + 2\text{NH}_3 + 3\text{H}_2$ .

A similar explanation may be given for the catalysis of hydroxylamine by platinum black (Tanatar, A., 1902, ii, 386, 495). The equation given above indicates a reaction of the fourth order for this decomposition, but the author's study of the velocity shows that the reaction is of the first order, and that it is the result of a number of simple reactions.

The mechanisms of the catalyses of azoimide (Cooke, P., 1903, 213) and ammonium nitrite (Vondráček, A., 1904, ii, 390) are also discussed.

T. H. P.

**Catalytic Actions at Solid Surfaces. V. Rate of Change Conditioned by a Nickel Catalyst and its Bearing on the Law of Mass Action.** E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1920, [A], **98**, 27—40. Compare this vol., ii, 422, 423).—The curves representing the hydrogenation of methyl cinnamate, anethole, and safrole at  $140^\circ$  and  $180^\circ$  in the presence of nickel have a form for 60—80% of their length represented by  $K = v/t$ , which indicates complete hydrogenation. In the case of isoeugenol and coumarin, the hydrogenation curves show a transition from a linear to a logarithmic curve. In the case of ethyl cinnamate, instead of passing a continuous stream of hydrogen over the catalyst, the tube was closed at one end; under these conditions, the results show: (i) with increasing purity of hydrogen, the ratio,  $v/t$ , approaches the constancy characteristic of hydrogenation in a continuous stream of hydrogen; (ii) the values of  $K' = 1/t \log V'/(V' - v)$  increase throughout, but become more nearly concordant as the purity of the hydrogen decreases. As the purity of the hydrogen and the speed of the action, measured by  $v/t$ , increase, the absolute value of the constant,

$$K'' = 1/t \log V''/V'' - v,$$

falls, that is, the rate at which the gas space becomes filled with impurity is smaller the purer the hydrogen. The hydrogenation curve of linseed oil shows an initial linear portion of about 30% of the whole curve, which corresponds with the hydrogenation of all the linolenin and most of the linolein; a very abrupt curvature then sets in, and this is followed by an approximately linear curve at a much lower slope. These experiments were carried out with 200, 300, and 400 grams of oil, and of 0.45 and 1.5 grams of

nickel. They show: (i) that the factor  $v/t$  depends on the mass of nickel present, (ii) the impurities in the oil gradually affect the catalyst, and (iii) with the smaller quantity of nickel the rates are practically the same for quantities of 200 and 300 grams of oil, but with 400 grams the linear portion of the curve is shortened, owing to the increased effect of the impurity.

It is shown that the hypothesis of unstable intermediate compounds between catalyst and reacting substances offers a reasonable explanation of the mechanism of "so-called" heterogeneous catalytic actions, and in particular for reactions of the types: (i) Action of enzymes on sugar derivatives in aqueous solution. (ii) The Sabatier catalyses of organic compounds in the presence of finely divided metals or metallic oxides, including hydrogenation and dehydrogenation, hydration and dehydration, formation of ethers and ketones, the specific action of finely divided metals on the vapours of aliphatic acids, and the combined dehydration and condensation processes effected by certain metallic oxides, leading to the production of ethers, amines, mercaptans, and esters from alcohols and phenols. (iii) The interaction of carbon monoxide and steam conditioned by various solid substances. J. F. S.

**Catalytic Activity of Copper.** I. W. G. PALMER (*Proc. Roy. Soc.*, 1920, [A], **98**, 13—26).—The mechanism of the catalytic oxidation of ethyl alcohol and isopropyl alcohol by metallic copper has been studied at temperatures up to  $320^{\circ}$ . It is shown that in no circumstances, even when the copper is alloyed with zinc, does electrolytic copper exert any influence on either of these alcohols. The oxidation is effected by copper produced by the reduction of copper oxide. The reaction has been carried out in such a way that the rate is automatically registered by the liberated hydrogen. In the present case, the initial period of the reaction alone has been considered. The experimental facts are best interpreted by assuming that alcohol is selectively adsorbed by copper from a mixture of alcohol and aldehyde vapours, so that during dehydrogenation the surface of the copper is covered by a layer of alcohol molecules, and adsorption and consequent destruction of the aldehyde prevented. If it be supposed that dehydrogenation of alcohol involves three stages, (i) adsorption of alcohol molecules over the surface of the copper, (ii) activation of certain alcohol molecules by absorption of energy, and (iii) evaporation of acetaldehyde and hydrogen from the adsorption surface into the alcohol stream flowing past the catalyst, then the process bears a close physical analogy to the escape of ions from a heated solid.

J. F. S.

**Conditions of Stability of Atoms.** FÉLIX JOACHIM DE WISNIEWSKI (*Arch. Sci. phys. nat.*, 1920, [v], **2**, 301—308).—A mathematical paper in which the stability of atoms of the Bohr type is derived from the assumption that the electrical potential energy of the atom is a positive function.

J. R. P.

**Constitution and Configuration of the Atom.** EMIL KOHLWEILER (*Zeitsch. physikal. Chem.*, 1920, **94**, 513—541).—A theoretical paper in which the views recently advanced by the author on the constitution and configuration of the atoms (A., 1918, ii, 286, 304; 1919, ii, 21) are extended and modified with the object of making the hypothesis include all the elements, particularly those of the rare earths. On the basis of the present hypothesis, a spatial representation of the periodic system is developed which arranges the elements according to a cascade system, in which the steps from one plane to the next are occupied respectively by cobalt and nickel, rhodium and palladium, the metals of the rare earths, and iridium and platinum. J. F. S.

**Structure of the Atomic Nucleus.** E. GEHRCKE (*Sitzungsber. Heidelberger Akad. Wiss., Math.-naturwiss. Kl.*, [A], 1919, pp. 19; from *Chem. Zentr.*, 1920, iii, 169—170).—In continuation of the models developed previously for the lithium, glucinum, boron, and carbon atoms (this vol., ii, 241), the author now puts forward structures for the atomic nuclei of the other elements to the end of the periodic scheme. The fundamental hypothesis is that the atomic nuclei of the higher elements are merely repetitions of those of a lower horizontal series of the periodic system, with the difference that the nucleus is surrounded by a ring of  $\alpha$ -particles. Thus, for example, the atomic nucleus of sodium is identical with a lithium nucleus surrounded by a ring composed of four  $\alpha$ -particles, whilst, similarly, the potassium nucleus is identical with a sodium nucleus surrounded by a ring of four  $\alpha$ -particles. Isotopes are possible for several atoms which differ from one another by an  $\alpha$ -particle in the ring enclosing the central nucleus. The number of  $\alpha$ -particle rings is considerable in the case of the higher elements. Every element would thus appear as a compound of a primal element,  $H^+$ , and electron, arranged according to a systematic and not too complicated plan. Order is thus introduced into the relationship between atomic weight and atomic number, and explanations are found for a lengthy series of empirical observations, such as the chemical similarity of the rare earths, the spaces in the periodic system, etc. H. W.

**Atomic Weights and Atomic Numbers.** STEPHEN MIALl (*Chim. et Ind.*, 1920, **4**, 189—192).—If graphs are plotted of which the ordinates represent atomic weights and the abscissæ the atomic numbers, that is, the positions of the elements in the periodic system, the series form nearly parallel curves. For the group of elements helium to nickel, and copper to tungsten, the curves are represented by the equation  $y = 2x + a$ , and for the group platinum to uranium by  $y = 3x + a$ . The lack of relationship between atomic weights and the properties of elements is assumed to be due to the factor  $a$ , which is known as the "inert weight"; the "active weight" of the atom determines the valency of the element, and not necessarily its chemical activity. Hydrogen does not conform



to the equation  $y=2x+a$ ; it may be represented by  $y=x$  or  $y=\frac{1}{2}x+\frac{1}{2}$ , but probably its atom contains no inert weight.

The graphs indicate that 2.5 units of the atomic weight are normally active, whilst one unit may be chemically inactive. Assuming the atoms to consist of particles equal to 0.5 of unity, it is probable that one particle is active, and that two particles may be either active or inactive. The equation  $y=Mx+a$  represents the atomic weights of all the elements,  $x$  being the atomic number and  $a$  a small whole number, the properties of the elements being independent of  $a$ .

W. J. W.

**Periodic System of the Elements in the Light of the Theory of Radioactive Degradation.** F. KIRCHHOFF (*Zeitsch. physikal. Chem.*, 1920, **94**, 257—262).—A theoretical paper in which the position in the periodic system and the possible genesis of the elements are considered in the light of the known facts of radioactive degradation. It is shown that the atomic weights,  $A$ , of the more stable elements, which are functions of the atomic number,  $M$ , and  $I$ , the number of nucleus electrons, in that  $A=2(M+I)$ , are periodic functions of  $I$ , since in certain parts of the periodic system  $A$  remains practically constant, and then commences to change regularly, and this reappears periodically.

J. F. S.

**Deduction of the Smoluchowski Formula of Spatial Partition of Particles in a Kinetic Field.** R. LORENZ and W. EITEL (*Zeitsch. physikal. Chem.*, 1920, **94**, 254—255. Compare A., 1914, ii, 451).—A correction of an intermediate stage in the deduction of the Smoluchowski formula previously published (*loc. cit.*).

J. F. S.

**Metastability of the Elements and Compounds as a Consequence of Enantiotropy or Monotropy. I.** ERNST COHEN and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1920, **94**, 450—464. Compare A., 1916, ii, 183).—A theoretical paper in which reasons for the failure of other workers in reproducing the authors' previous work on metastable varieties of metals are enumerated. It is also pointed out that metastable varieties of elements and compounds are of much more frequent occurrence than has been generally believed. A general discussion of the conditions under which such metastable varieties may be obtained is entered into, and particular stress is laid on the influence of minute traces of impurities.

J. F. S.

**A Method for the Experimental Proof of the Molecular Theory and the Avogadro-Loschmidt Number.** A. VON SZENT-GYÖRGYI (*Zeitsch. physikal. Chem.*, 1920, **95**, 247—250).—A method is indicated by which the Avogadro number may be experimentally determined. The method consists in adding to an albumin suspension of known content various solutions of known concentration of aluminium chloride, and examining the charge

on the particles. When exactly the correct quantity of aluminium chloride has been added, so that the particles all change the cataphoresis from positive to negative, it is possible to calculate the Avogadro number on the assumption, which is substantiated, that one ion discharges one albumin particle. J. F. S.

**Nature of the Chemical Bond ; an Attempt to Find a Common Cause for the Conceptions ; Auxiliary Valency and Molecular Bond.** F. HOCHEDER (*Zeitsch. physikal. Chem.*, 1920, **94**, 129—148).—A theoretical paper in which an hypothesis is put forward to explain the origin of subsidiary valencies, and, at the same time, to account for the formation of double compounds, complexes, and hydrates. It is assumed, in keeping with Bohr's hypothesis, that the ordinary chemical bond is due to an oscillating electron between the two atoms concerned; this is regarded as an electric current flowing in a close circuit in which the atoms concerned lie. When two such circuits lie parallel to one another, there will naturally be an attraction set up between them, and this could well be powerful enough to hold the two compounds together, that is, a molecular compound would be formed. For such a compound to be stable, it is necessary that the bonds in the individual compounds should be parallel, and that the current in each flowing at the same rate and in the same direction, that is, the periodicity of the electron oscillation is the same in both cases. The hypothesis is illustrated in connexion with a number of well-known double compounds, and it is discussed in connexion with Werner's co-ordination theory. As will be seen, a new type of spatial structure is involved in this hypothesis. J. F. S.

**Negative Valencies.** D. STRÖMHOLM (*Zeitsch. anorg. Chem.*, 1920, **111**, 237—242).—A theoretical paper in which the valencies of negative elements are considered. It is pointed out that when a negative element forms compounds in which it acts with different valencies, these always differ by two, that is, the valencies of negative elements are always saturated in pairs. This is to be explained by assuming that in the negative elements the valency electrons are grouped together in pairs. The valency figure of 8 which dominates the negative valencies is therefore to be regarded as made up of four pairs of electrons, which constitute a completely saturated system. This is governed by the tetrahedral symmetry, and the stereochemical data show that, in the case of those elements which can enter into combination by their negative valencies, the symmetry relationships are determined by the tetrahedron. J. F. S.

**Chemical Concepts of the Ancient Orientals.** Y. H. CHEN (*Science [China]*, 1920, **4**, 262—284).—Chemical knowledge in ancient China seems to have attained a rank comparable to that reached in Egypt. The four elements, earth, fire, air, water, formed the basis of a later chemical philosophy, which was

developed quite independently of the Occident. Theories were developed similar to those of Aristotle and of the earlier iatro-chemists. The Orient also produced a system of iatro-chemistry founded on the "Ben Tsao" written in 2838 B.C. This medical chemistry ceased its development from about 1200 A.D.

CHEMICAL ABSTRACTS.

**An American Edition of the Elementary Treatise of Chemistry by Lavoisier, published at Philadelphia in 1799.**

GRAHAM LUSK and JEAN LE GOFF (*Bull. Soc. chim.*, 1920, [iv], 27, 667—673).—A brief description of the various French editions of Lavoisier's work, and the subsequent English, Spanish, Italian, and Dutch translations, together with an account of an edition published in Philadelphia in 1799.

W. G.

**Improved Form of U-Tube.** E. R. DOVEY (*Analyst*, 1920, 45, 333).—The two limbs of the U-tube are brought together so that the rims at the top are in contact; the bend at the bottom of the tube is constricted, and a perforated Gooch disk is placed at the bottom of each limb.

W. P. S.

**Extraction Apparatus with Vapour Stirring.** P. WAENTIG (*Text. Forsch.*, 1920, 2, 61—62; *Chem. App.*, 1920, 7, 92—93; from *Chem. Zentr.*, 1920, iv, 265).—In order to allow the vapours of the boiling liquid to enter the extraction space, and thus to utilise their latent heat in the Soxhlet apparatus, the lower tube of the latter is sunk so deeply into the liquid in the boiling flask that its open end becomes clear of the surface of the liquid only when the extraction tube is filled almost to the level of the top of the syphon tube. To allow the vapour from the boiling liquid to pass into the syphon tube, the latter is somewhat lengthened, and terminates just above the level of the boiling liquid in the flask.

H. W.

**Air-oven Thermo-regulator.** H. M. ATKINSON (*J. Soc. Chem. Ind.*, 1920, 39, 298r).—A cylindrical float, loaded slightly with mercury and having its upper end in the form of a capillary, is contained in one limb of a U-tube filled partly with mercury. The capillary extends upwards into a tube passing through the cork closing this limb of the U-tube, the shoulder of the float and the end of the tube being ground to form a gas-tight joint when the float rises. The gas enters through a side-tube above the mercury-level, passes between the neck of the float and the tube, then into the latter and thence to the burner. The other limb of the U-tube connects with a bulb in the oven. When the float rises and cuts off the gas supply, a small quantity of gas is allowed to pass through a hole in the side of the float and escapes through the capillary to the burner, the capillary thus acting as a by-pass.

W. P. S.

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## Inorganic Chemistry.

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**Preparation of Ammonia-free Water.** GERALD C. BAKER (*J. Ind. Eng. Chem.*, 1920, **12**, 798—799).—Water free from ammonia may be obtained by passing distilled water through a moderately deep layer of permutite (a complex hydrated sodium aluminium silicate); a layer 30 cm. deep and 20 cm. in diameter will remove the ammonia from 450 litres of water. The activity of the permutite may be regenerated by treatment with 10% sodium chloride solution. The disadvantage of the method is that it gives a water of higher mineral content. W. P. S.

**Rate of Decomposition of Hydrogen Peroxide in the Presence of Iron Ions.** JOSEPH VON BERTALAN (*Zeitsch. physikal. Chem.*, 1920, **95**, 328—348).—The rate of decomposition of hydrogen peroxide at 40° has been determined in the presence of ferrous sulphate or ferric sulphate and a little free sulphuric acid (0.01*M*). The reaction occurs in all cases as a typical unimolecular catalytic process. The velocity of reaction in acid solutions and in the presence of either ferrous or ferric ions is directly proportional to the concentration of the hydrogen peroxide and that of the iron ions, and inversely proportional to the hydrogen-ion concentration or the concentration of the free acid. The velocity of the reaction is entirely independent of the state of oxidation of the iron ions, and the catalytic action depends on the total amount of iron present, no matter what its state of oxidation. The temperature-coefficient of the reaction is 3.25 for 10°. J. F. S.

**Solubility of Halogens in the Corresponding Hydracids and Alkali Salts. II.** E. OLIVERI-MANDALÀ (*Gazzetta*, 1920, **50**, ii, 89—98. See this vol., ii, 542).—The solubilities of chlorine in sodium chloride solutions and hydrochloric acid, and that of bromine in hydrochloric and hydrobromic acids, have been measured.

The results confirm the observation that the solubility of chlorine is greater in hydrochloric acid than in water, whereas the presence of sodium chloride diminishes the solubility in water by amounts increasing with the proportion of salt present. The coefficient of solubility of the chlorine diminishes as the concentration of sodium chloride increases, but the expression  $(\alpha' - \alpha)/M^{\frac{1}{2}}$  gives constant values,  $\alpha'$  and  $\alpha$  representing the coefficient of absorption of chlorine in water and sodium chloride solution respectively, and  $M$  the concentration of the salt in gram-mols. per litre of solvent. This empirical formula has been verified (Gordon, A., 1896, ii, 154) for the solubility of indifferent gases in aqueous solutions of electrolytes, so that chlorine behaves differently from the other halogens, which exhibit almost the same solubility in solutions of the corresponding hydracids and in those of the alkali salts. T. H. P.

**Action of Light on Moist Chlorine.** ERNST RADEL (*Zeitsch. physikal. Chem.*, 1920, **95**, 378—383).—Using the ultra-microscopic method, the reaction between chlorine and hydrogen has been studied. It is found that when moist chlorine is illuminated an induction period is set up which varies between 1/100 sec. and 30 secs., after which a fine fog is produced which rapidly forms drops. On removing the light the particles become smaller, and eventually disappear. The same effect is observed when the chlorine is ionised by a spark from an induction coil or by the light from a Tesla transformer. Radiation from polonium or radium bromide has the same effect, but much weaker. J. F. S.

**Concentration of the Lighter Isotope of Iodine.** EMIL KOHLWEILER (*Zeitsch. physikal. Chem.*, 1920, **95**, 95—125).—In an earlier paper (this vol., ii, 610) the author has shown that in all probability five isotopes of iodine exist which have atomic weights 122, 124, 126, 128, 130, depending on their origin. This involves differences varying between -3.88% and +2.43% from the mean value, 126.92, of the atomic weight. Vapour density determinations have been carried out by the Dumas method with iodine which has been twice sublimed, thrice sublimed, recrystallised from carbon disulphide, separated by diffusion, and fractionated. Ten experiments with twice sublimed iodine give an atomic weight which has a mean divergence of 2.04% from the accepted value; eight experiments with fractionated iodine give a mean divergence of 1.33%. Of twenty-seven experiments, not one gives atomic weights which are equal to or less than the accepted value. The lowest value obtained for the atomic weight is 128.22. An apparatus is described by means of which a possible separation of the isotopes may be brought about by diffusion. J. F. S.

**Preparation of Iodic Acid and its Anhydride.** ARTHUR B. LAMB, WILLIAM C. BRAY, and WALTER J. GELDARD (*J. Amer. Chem. Soc.*, 1920, **42**, 1636—1648).—A simple and rapid method has been developed for the preparation of iodine pentoxide, which depends on the oxidation of iodine to iodic acid by means of 24—26% chloric acid solution, the evaporation of the solution and the dehydration of the iodic acid. The product is pure white, has practically 100% of the oxidising value, and contains no detectable impurities except traces of water and barium iodate. It is decidedly more stable towards heat than iodic anhydride as ordinarily prepared, and, therefore, has decided advantages for use in the analysis of small quantities of carbon monoxide in air. The yield of pentoxide is almost theoretical. In the preparation a small excess (3%) of chloric acid is used; this ensures the complete removal of the hydrochloric acid formed during the oxidation process, which otherwise would reduce the iodic acid during evaporation. When this small excess of chloric acid is used, the net result of the oxidation is expressed by the equation  $I_2 + 2HClO_3 = 2HIO_3 + Cl_2$ . The mechanism of this reaction undoubtedly does not correspond with

a direct replacement of chlorine by iodine. The chloric acid solution is made by the direct action of sulphuric acid on barium chlorate solution. There is no decomposition of the chloric acid, and the only loss is the small amount of solution absorbed by the barium sulphate. This method of preparation presents no difficulties on the manufacturing scale.

J. F. S.

**Colloidal Sulphur.** PAUL BARY (*Compt. rend.*, 1920, **171**, 433—435).—Colloidal sulphur in the form of a limpid liquid is a hydrophile colloid, capable of absorbing water. This absorption is favoured by the presence in solution of small amounts of salts of univalent metals, whilst it is prevented by the action of salts of bivalent metals. Such colloidal sulphur is not pure sulphur, but a compound containing sulphur in a highly polymerised state. The compounds are easily dissociable, and only exist in aqueous medium in the presence of substances which limit their decomposition. When the swelling of the granules, due to the absorption of water, becomes small the granules lose their transparency and the liquid becomes milky and loses its stability.

W. G.

**Freezing Points of Mixtures of Sulphuric and Nitric Acids.**

W. C. HOLMES (*J. Ind. Eng. Chem.*, 1920, **12**, 781—783).—The freezing points of mixtures of sulphuric and nitric acids containing 0 to 50% of the latter were determined in test-tubes immersed in an insulated bath of ether and carbon dioxide snow, and the results plotted as curves. In the case of mixtures with a total acidity of 100% the freezing point reached a minimum ( $-18.2^{\circ}$ ) when 5.4% of nitric acid was present, and a maximum ( $+2.3^{\circ}$ ) with 10.8% of nitric acid. The curve closely resembled that of sulphuric acid and water, which reached a minimum ( $-34^{\circ}$ ) with 8.4% of water, and a maximum ( $+8^{\circ}$ ) with 15.5% of water. It is probable that at the maximum point in the nitric acid mixtures a definite compound,  $5\text{H}_2\text{SO}_4, \text{HNO}_3$ , is present, whilst the minimum point coincides with a compound of the approximate composition  $5\text{H}_2\text{SO}_4, \frac{1}{2}\text{HNO}_3$ . In the determinations with mixtures of a total acidity of 95% the freezing point fell to  $-41.0^{\circ}$  with 2.35% of nitric acid, then rose to  $-11.0^{\circ}$  with 9.75%, and fell again to  $-41.3^{\circ}$  with 49.09%. With mixtures of a total acidity of 103% the minimum ( $-12.3^{\circ}$ ) was reached with 8.15% of nitric acid and the maximum ( $+10.5^{\circ}$ ) with 15.52%. The last two series of results were complicated by the presence of water and sulphur trioxide respectively.

C. A. M.

**Vapour-pressure Curves of Solid and Liquid Selenium near the Melting Point.**

L. E. DODD (*J. Amer. Chem. Soc.*, 1920, **42**, 1579—1594).—The sublimation curve for crystalline selenium (hexagonal) has been determined over the temperature range  $190$ — $215^{\circ}$  by the method of molecular flow. By the same method data for the vaporisation curve for the liquid of vitreous amorphous selenium have been obtained over the temperature range

220—235°. The relation between vapour pressure and temperature for selenium over the temperature range considered and on the basis of a diatomic vapour may be expressed by a simple exponential equation,  $p = c_1 \cdot e^{c_2/T}$ , where  $T$  is the absolute temperature. On the basis of a diatomic vapour the results appear to locate the melting point at 217.4°, and give a pressure value at the melting point of 12.68 bars (0.00954 mm.), and slope values for the  $p$  and  $T$  curves at the melting point of 1.050 bars/degree (0.000767 mm./degree) for the crystals, and 0.573 bar/degree (0.000431 mm./degree) for the liquid. The slope at the melting point was thus found to be greater for the solid than for the liquid, as required by thermodynamics, and as found for other substances. The difference between the two slopes is 0.477 bar/degree (0.000358 mm./degree) on the basis of a diatomic molecule. From Clapeyron's first latent heat equation, the three latent heats at the melting point were calculated on the basis of a diatomic vapour, as follows: latent heat of vaporisation, 135.5; latent heat of sublimation, 219.4; and latent heat of fusion, 83.9 cal./gram. Since the vapour density at the experimental temperatures is unknown, the three latent heats, as well as the pressure at the melting point, and the slopes of the  $p$  and  $T$  curves at the melting point, have been calculated on the basis of 4, 6, 8, 10, and 12 atoms per molecule of vapour. The calculated latent heat values vary inversely as these numbers. These results are not out of keeping with the requirements of the Kirchhoff equation, based on thermodynamics, relating vapour pressure and temperature, but they do not give positive evidence that this equation is applicable to selenium, as would be expected from the limited temperature range even if that relation should apply.

J. F. S.

**Tellurium Nitrite.** FELIX VON OEFELE (*Pharm. Zentr.-h.*, 1920, **61**, 491—492).—By the action of nitric acid on tellurium, under certain conditions, namely, using large quantities of material and a high column of liquid (not less than 50 cm.), tellurium nitrite was obtained as a flesh-coloured precipitate, which could be dried at 100° without decomposition. At higher temperatures it decomposes, leaving a residue of yellow tellurium dioxide. E. H. R.

**Rutherford's Experiments on the Subdivision of the Nitrogen Nucleus.** W. LENZ (*Naturwiss.*, 1920, **8**, 393; from *Chem. Zentr.*, 1920, iii, 300).—The priority in the explanation of the deficit in the atomic weight by the theory of the lag of energy should be ascribed to Swinne, and not, as previously (this vol., ii, 427), to Harkins and Wilson. H. W.

**Determination of the Electrolytic Potential and Over-voltage of Arsenic.** VINCENT B. MARQUIS (*J. Amer. Chem. Soc.*, 1920, **42**, 1569—1573).—The normal potential of an arsenic electrode has been calculated from *E.M.F.* measurements of cells of the type  $\text{Hg}, \text{HgCl} | \text{LiCl} \text{ in absolute alcohol} || \text{AsCl}_3$  (0.176*M*) in

absolute alcohol|As. This cell had an *E.M.F.* of 0.153 volt, which, making use of the Rideal and Roderburg method of calculation, is equivalent to 0.040 volt for the arsenic-alcohol potential and 0.111 volt for the arsenic-water potential. From this, the electrode potential, 0.138 volt, is obtained, which places arsenic between hydrogen and copper in the electrode series. The molecular conductivity of arsenic trichloride in alcohol has been determined at 20°, and concentration-conductivity curves drawn. The dissociation of arsenic trichloride in alcohol solution is 20.6% in 0.176*M*-solution. Conductivity determinations also show that there is no appreciable hydrolysis of arsenic trichloride in alcohol solution, but that there is a slight combination with the solvent. The hydrogen overvoltage on arsenic electrodes has been determined by both the open-circuit and closed-circuit methods. The former method gives a value 0.379 volt and the latter 0.478 volt.

J. F. S.

**A Decolorising Carbon.** JOSEPH C. BOCK (*J. Amer. Chem. Soc.*, 1920, **42**, 1564—1569).—The decolorising action of a vegetable carbon, sold under the name Norit, on biological fluids has been investigated. Norit is found to extract uric acid completely from urine; creatinine is extracted to a large extent, carbamide, total nitrogen and phosphates are removed to a considerable extent, and ammonia-nitrogen, chlorides and dextrose are slightly removed. Bouillon cultures, on shaking with norit for a few seconds and subsequently keeping in contact for three to four minutes, showed a marked decrease in the number of bacteria. Freundlich's simple adsorption formula holds exactly for the adsorption of total nitrogen and creatinine, and probably holds for dextrose. When several substances are present in a given solution, each one of them is adsorbed less than when they are present separately. Thus urine containing 1.77% of dextrose loses no sugar on treatment with norit, whereas a 0.77% aqueous solution of dextrose loses 16.88% of its sugar after the same treatment. Lactose is removed from milk by norit. Washed norit (ash, 2.18%) is more efficient than commercial norit (ash, 5.13%) as an adsorbent.

J. F. S.

**The Strength of Aqueous Carbonic Acid Solutions at High Pressures.** OTTO HÄHNEL (*Centr. Min.*, 1920, 25—32).—Experiments were made to determine the solubility of carbon dioxide in water at higher pressures, and the electrical conductivity of the solutions. The solutions were prepared by saturating water with carbon dioxide in an autoclave of large capacity. When the pressure had been measured, a quantity of the saturated solution was removed to a special eudiometer, and the excess of gas allowed to escape from the solution at atmospheric pressure, the volume of gas and water being then measured. Determinations were made at 0° at pressures up to 38 atm. and at 15° up to 52 atm. At 0° and 38 atm., a saturated solution contains 7.44% by weight of carbon dioxide, and at 15° and 52 atm., 5.44%. Henry's law



is not obeyed, for the rate of increase in solubility diminishes with increasing pressure. The electrical conductivity of the solutions is very low; thus, a 2.99% solution, at 15° and 20 atm., has a conductivity only half that of a 0.3% solution of acetic acid. It has been shown, however, by Thiel and Strohecker (A., 1914, ii, 361) that in a 0.038% solution of carbon dioxide at 4°, only 0.56% exists in the hydrated form, as  $\text{H}_2\text{CO}_3$ . If the same holds true at higher concentrations and pressures, the true concentration of carbonic acid in a saturated solution at, say, 15° and 52 atm., is 0.027%, and its conductivity,  $1.98 \times 10^4$ , is of the same order as that of formic acid at a similar concentration. Carbon dioxide must, then, be classed with the stronger acids, a conclusion which accords fully with the known activity of the acid in rock formation and degradation.

E. H. R.

**Preparation of Thiocarbonyl Tetrachloride.** PERCY FARADAY FRANKLAND, FREDERICK CHALLENGER, and DOROTHY WEBSTER (*J. Soc. Chem. Ind.*, 1920, **39**, 256—257T).—For the preparation of thiocarbonyl tetrachloride on a large scale, 4 grams of iodine are added to 2 kilos. of carbon disulphide dried over calcium chloride, dry chlorine is passed in, the temperature not being allowed to exceed 20°, until the increase in weight corresponds with the absorption of five atomic proportions of chlorine, when the reaction mixture is run, in a thin stream, into hot water through which steam is being blown. Sulphur chloride is thus decomposed, and thiocarbonyl tetrachloride distils over. The latter is again distilled with steam, then dried over calcium chloride, and fractionally distilled until the temperature reaches 140°. The residue in the flask is the required thiocarbonyl tetrachloride, and by this process a 60% yield may be obtained. It should be noted that thiocarbonyl tetrachloride is completely decomposed by contact with metallic iron at the ordinary temperature. W. G.

**Behaviour of Concentrated Alkali Chloride Solutions in Presence of Alkali Hydroxides.** CH. CHOROWER (*Zeitsch. angew. Chem.*, 1920, **33**, 201—203).—The author has investigated the solubility of alkali chlorides in liquors derived from the treatment of vinasses ash with lime and barium hydroxide. The composition of an experimental liquor was: Cl, 3.559; OH, 0.9278; K, 4.792; Na, 0.933; S, 0.0594;  $\text{SO}_4$ , 0.0321;  $\text{CO}_3$ , 0.0705%. The liquor was evaporated in quantities of 4 litres, and boiling-point determinations were made at various stages when deposition of salts ceased. The density was then determined in a modified pycnometer, and the samples analysed. Six samples tested from quantities of 15, 20, 25, 35, 41, and 48 litres, with boiling points 110°, 111°, 112°, 115°, 116°, and 118°, showed increasing densities from 1.295 to 1.370. The chlorine ions diminished from 12.58 to 7.661, and potassium ions remained nearly constant at approximately 17, but all the other ions gave progressively rising values. The author discusses the phenomena by the application of the theory of mass action and of the phase rule.

W. J. W.

**Oxidation of Potassium Plumbite to Plumbate by means of an Alternating Current.** FRANZ JIRSA (*Zeitsch. physikal. Chem.*, 1920, **94**, 1—5).—The electrolysis of a solution (*N*) of potassium hydroxide between lead electrodes by means of an alternating current of 49 periods brings about the formation of potassium plumbite as the only product. It is shown that the plumbite may be electrolytically oxidised to plumbate if electrodes of suitable metals are used. The metals copper, silver, gold, cadmium, magnesium, mercury, nickel, iron, platinum, and palladium when used as electrodes with alternating current effect the oxidation but no oxidation occurs when lead, bismuth, cobalt, thallium, or carbon is used. The nature of the electrode is also determinative of the product of the oxidation; under the same conditions (40 grams of potassium hydroxide and 4.5 grams of lead oxide per litre) with palladium electrodes, yellow lead sesquioxide separates and lead metaplumbate is formed, whilst with nickel or iron electrodes a dark brown powder separates, which is the dioxide, and the yellow plumbate is not formed. It is shown also that, even with electrodes which are capable of effecting oxidation, oxidation does not always take place; under certain conditions, reduction, or even oxidation and reduction, may occur. The disintegration of the electrodes is an accelerating factor of the reaction. J. F. S.

**Sodium Phosphide.** E. TOMKINSON and G. BARKER (*Chem. News*, 1920, **121**, 104—105, 177).—When sodium is heated with red phosphorus, amongst other products, a grey mass is obtained, which is acted on violently by water, giving spontaneously inflammable hydrogen phosphide. With yellow phosphorus under suitable conditions, a white, crystalline product is obtained. W. G.

**The Third and the Fourth Dissociation Constants of Pyrophosphoric Acid and the Examination of the Purity of Sodium Pyrophosphate.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1920, **57**, 474—481).—The hydrogen-ion concentration of dilute solutions of sodium pyrophosphate was determined colorimetrically by comparing the colour change of thymolphthalein in these solutions and in mixtures of carbonate and hydrogen carbonate solutions of known  $p_H$  value. From the results, a mean value of  $4.6 \times 10^{-9}$  for the fourth dissociation constant was calculated. Further measurements with mixtures of pyrophosphate and small quantities of hydrochloric acid, so as to give the ion  $HP_2O_7'''$  in presence of  $P_2O_7''''$ , led to the result  $K_4 = 3.6 \times 10^{-9}$ , with certain assumptions as to the degree of dissociation of the solution. The third dissociation constant was determined in a similar way by measurements in mixed solutions of  $Na_3HP_2O_7$  and  $Na_2H_2P_2O_7$ , the value  $K_3 = 7.6 \times 10^{-7}$  being obtained. W. S. M.

**Metastability of the Metals as a Consequence of Allotropy and its Significance for Chemistry, Physics, and Technics.** IV. ERNST COHEN and H. B. BRUINS (*Zeitsch. physikal. Chem.*, 1920, **94**, 443—449. Compare A., 1914, ii, 52, 202, 332, 652, 799; 1915, ii, 52, 83, 417, 471, 565, 634; 1916, ii, 183).—A repetition

of earlier experiments in which a change in density of silver and cadmium was found after keeping under solutions. This change has been attributed to the adsorption of water or solution. The present experiments were undertaken to ascertain whether or no the metal does contain water after the treatment. The results show that whilst water is contained in the metals to the extent of 0.1—0.001%, the amount is so small as to be without effect on the density, and consequently can play no part in the changes previously observed. J. F. S.

**Binary System Åkermanite-Gehlenite.** J. B. FERGUSON and A. F. BUDDINGTON (*Amer. J. Sci.*, 1920, [iv], **50**, 131—140. Compare Ferguson and Merwin, A., 1919, ii, 459).—The binary system åkermanite ( $2\text{CaO}, \text{MgO}, 2\text{SiO}_2$ )—gehlenite ( $2\text{CaO}, \text{Al}_2\text{O}_3, \text{SiO}_2$ ) has been studied by the quenching method, and the curves of the solid and the liquid phases constructed. The system is found to consist of a complete series of solid solutions with a minimum melting point,  $1388^\circ$ ,  $70^\circ$  below that of åkermanite ( $1458^\circ$ ). The refractive index and general optical characteristics have been determined for the intermediate compositions, and are found to be a continuous function of the composition. Crystals of a certain intermediate mixture are isotropic for sodium light, and constitute a transition phase from crystals of positive optical character to those of negative optical character. Zoned crystals showing material of both positive and negative optical character in the same crystal were obtained. These are analogous, in this respect, to certain natural melilite crystals which have been previously described. The densities of crystals of åkermanite, gehlenite, and several intermediate mixtures have been determined and found to confirm the isomorphous character of the system. Åkermanite was found to show the unusual feature of its glass having a greater density (2.955) than the corresponding crystals (2.944) at  $25^\circ$ . J. F. S.

**Piezo-chemical Studies. XVI. Experimental Proof of Braun's Law by an Electrical Method.** ERNST COHEN, C. W. G. HETTERSCHIJ, and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1920, **94**, 210—232. Compare A., 1919, ii, 321).—Braun's law has been experimentally examined for the case of cadmium iodide by the electrical method of Cohen and Sinnige (A., 1909, ii, 981), and it is shown that within the limits of the experimental error this law accurately represents the experimentally found facts. To arrive at this conclusion the following data have been obtained for cadmium iodide: temperature-coefficient of the solubility,  $(\partial x / \partial T)_{30.0^\circ} = +0.1003 \pm 0.001$  gram per 100-gram solution/degree; pressure-coefficient of the solubility,  $(\partial x / \partial \pi)_{30.0^\circ} = -0.00390 \pm 0.0002\%$ /atm.; the fictitious volume change,  $\Delta V = 0.0191 \pm 0.0003$  c.c./gram, and the fictitious heat of solution,  $Q_{30.0^\circ} = 3.71 \pm 0.07$  gram-cal./gram. Substituting the first three of the above quantities in Braun's equation, the value of  $Q$  is found to be  $3.60 \pm 0.19$  gram-cal./gram. The determination of the pressure-coefficient of the solu-

bility indicates that this factor may no longer be regarded as negligibly small.  
J. F. S.

**Metastability of Elements and Compounds as a Consequence of Enantiotropy or Monotropy. III. Cadmium Iodide.** ERNST COHEN and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1920, **94**, 471—481. Compare this vol., ii, 620).—Cadmium iodide has been carefully examined, and it is shown that at temperatures between that of the melting point and ordinary temperature, it exists in two modifications which stand to one another in monotropic relations. Cadmium iodide obtained by crystallisation from solution or by sublimation is a mixture of  $\alpha$ - and  $\beta$ -forms in unknown quantities. The physical properties of cadmium iodide hitherto recorded, except those recorded by Cohen, Hetterschij, and Moesveld (preceding abstract), refer to a mixture of the  $\alpha$ - and  $\beta$ -forms of unknown composition.  
J. F. S.

**Melting Points and Thermoelectric Behaviour of Lead Isotopes.** THEODORE W. RICHARDS and NORRIS F. HALL (*J. Amer. Chem. Soc.*, 1920, **42**, 1550—1556).—The melting points of two isotopic varieties of lead, which differed by 0.8 in atomic weight, have been determined and found to differ by not more than 0.05°. From this result it may be assumed that the other kinds of lead not only have very nearly the same melting point, but also, since the sample consisting chiefly of lighter isotopes doubtless contained ordinary lead, that they mix or, better, mutually dissolve without affecting the melting point. The Seebeck thermoelectric effect produced at the junction of the two kinds of lead was determined and found to be zero. (See also A., 1916, ii, 250.)  
J. F. S.

**Disglomeration: a New Mode of Transformation of Solidified Metals.** A. THIEL (*Sitzungsber. Ges. gesamt. Naturwiss. Marburg*, 1920, i, 1—17; from *Chem. Zentr.*, 1920, iii, 227).—The allotropy of lead does not play any part in the transformation of lead according to Heller's experiments (A., 1915, ii, 634; compare also Cohen and Helder mann, A., 1915, ii, 456). Disglomeration (disintegration in consequence of the solution of the eutectic formed by lead and its impurities and located between the lead crystals) is a consequence of the chemical action of the dissolved nitrate and formation of lead nitrite. Disglomeration only occurs with solidified metals (copper in addition to lead). Formation of the lead tree is only observed when local, short-circuited, ionic concentration cells are developed. All types of lead which separate as the lead tree are crystallographically identical with that which has crystallised from the molten metal; the earlier explanation of the phenomenon as being due to allotropy is therefore excluded.  
H. W.

**Rate of Dissolution of Metallic Copper in Aqueous Ammonia.** EIICHI YAMASAKI (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, **9**, 169—220).—The copper was vigorously rotated with a con-

stant velocity in ammonium hydroxide, and a steady current of air passed through. Two chemical actions take place in the solution, the electrolytic dissociation of the copper and the autocatalytic reaction of cuprammonium compound in solution. The velocity of the former increases proportionally to the square root of concentration of free oxygen, and the rate of the latter to that of the cuprammonium compound. The total velocity is independent of the concentration of free ammonia and the nature of the anions. The dissolution velocity increases regularly to a maximum and then decreases again. The maximum is attained at a concentration of cuprammonium hydroxide, which is practically proportional to the concentration of free ammonia. The range of solution of copper is increased by the presence of an ammonium salt. A mathematical formula is obtained which represents the course of the reaction with sufficient accuracy. The velocity of dissolution is found to be roughly proportional to a two-thirds power of the rate of stirring. The temperature-coefficient is only 1.15, so that probably the velocity of reaction is chiefly determined by that of diffusion. Diffused daylight has no effect on the velocity. With the addition of hydroxylamine, dissolution takes place very slowly, probably due to the checking of the autocatalytic action of the dissolved copper. Sodium oleate has a retarding effect, and amalgamation considerably reduces the velocity. The effect of carbon monoxide is slight, but hydrogen peroxide increases the initial velocity of dissolution. The best conditions for the preparation of the solution of cuprammonium hydroxide are discussed on the basis of the present investigation in view of its importance in the manufacture of artificial silk.

T. H. B.

**Similarity in Micrographic Appearance Existing at Different States between Iron-Carbon Alloys (Steels), Copper-Tin Alloys (Bronzes with Tin), Copper-Zinc Alloys (Brasses), and Copper-Aluminium Alloys (Bronzes with Aluminium).** A. PORTEVIN (*Compt. rend.*, 1920, 171, 350—353).—In the case of copper-tin and copper-aluminium alloys the austenitic, martensitic, and troostitic states have previously been observed, as well as the two aspects of the eutectoid. For copper-zinc alloys the austenitic and troostitic states have been observed, and the author has now obtained microphotographs showing first the eutectoid resolved during cooling, and secondly the martensitic state for these alloys.

W. G.

**Chemical and Electrochemical Properties of Copper-Zinc Alloys Prepared by Melting or by Electrochemical Processes.** FRANZ SAUERWALD (*Zeitsch. anorg. Chem.*, 1920, 111, 243—279).—An account is given of the action of various reagents, such as solutions of cadmium sulphate, copper sulphate, sulphuric acid, hydrochloric acid, thallous sulphate, lead chloride, lead nitrate, and alkali sulphides, on alloys of zinc and copper prepared by various methods and of varying composition. The *E.M.F.* of alloys (100—18.4% Cu) against a solution of zinc chloride has also been measured, and the change with temperature ascertained. It is

shown that the behaviour of zinc-copper alloys is governed by the two factors which determine the chemical and electrochemical behaviour of mixed crystals, namely, the nature of the partition of the components and the mobility of the atoms in the crystal lattice. It is shown that the mixed crystals, obtained by melting, with ordered partition corresponding with the equilibrium conditions, have chemical and electrochemical properties at the ordinary temperature which to a large extent are independent of the concentration. This is to be attributed to the protecting action of the copper. The properties change sharply and suddenly only on the appearance of a new crystal form with a different lattice, whereby in the case of copper saturated with  $\gamma$ -crystals, the properties of the compound  $\text{Cu}_2\text{Zn}_3$  were observed. At  $380^\circ$ , where a considerable mobility of the atoms in the lattice exists, the electrochemical properties of the mixed crystals are dependent on the concentration, since the copper is no longer able to afford a protecting action. In the case of unordered atom partition, which is obtained by electrolytic deposition at the ordinary temperatures, the copper is only able to afford a very slight protecting action to the zinc. From this the simple relationship follows that the logarithm of the solution pressure of the zinc in alloys with unordered partition is proportional to the number of unprotected zinc atoms. The atom partition brought about by electrolysis is to a large extent dependent on the temperature, for it is shown that by the electrolysis of molten salts at  $300^\circ$  an alloy is obtained in which the atom partition is very nearly that of the equilibrium condition.

J. F. S.

**Topochemical Reactions. Formation and Behaviour of Copper Hydroxide.** V. KOHLSCHÜTTER and J. L. TTSCHER (*Zeitsch. anorg. Chem.*, 1920, **111**, 193—236).—A topochemical reaction is defined as one which depends on the relative position in space of the reacting groups or molecules. The present paper gives a long account of the various methods of preparation of copper hydroxide and the properties of the various products. In particular the loss of water from the hydroxide to form oxide and partly dehydrated hydroxides is considered. Four means of dehydrating copper hydroxide are considered: (i) thermal separation of water,  $\text{Cu}(\text{OH})_2 \rightarrow \text{CuO} + \text{H}_2\text{O}$ ; (ii) separation of water by osmotic pressure owing to the evaporation of the surrounding liquid; (iii) endosmotic drying of the hydrated compound on an anode; and (iv) water separation by internal neutralisation, due to amphoteric ionisation. The authors are of the opinion that the dehydration of copper hydroxide takes place according to the last-named method. The process is represented by the equations  $\text{Cu}(\text{OH})_2 \rightleftharpoons \text{Cu}'' + 2\text{OH}'$ ;  $\text{Cu}(\text{OH})_2 \rightleftharpoons \text{CuO}_2'' + 2\text{H}'$ ;  $\text{HO}' + \text{H}' \rightleftharpoons \text{H}_2\text{O}$ ; and  $\text{CuO}_2'' + \text{Cu}'' = 2\text{CuO}$ .

J. F. S.

**The Electro-affinity of Aluminium. III. The Acidity and Constitution of Aluminic Acid.** JAROSLAV HEYROVSKÝ (*T.*, 1920, **117**, 1013—1025).

**Hydrates of Aluminium Nitrate.** KENZO INAMURA (*J. Tokyo Chem. Soc.*, 1920, **41**, 1—8).—Mixtures of aluminium nitrate ( $18\text{H}_2\text{O}$ ), nitric acid, and water in various proportions are left for one to two days at  $25^\circ$ . After the equilibrium is established, the solution is separated from the residue, and aluminium, nitric acid, and water are estimated in the two fractions. The results are given in two tables and two curves, which show that in proper concentrations of nitric acid, at  $25^\circ$ , the nitrate produces three hydrates containing 18, 16, and 12  $\text{H}_2\text{O}$  respectively. The first hydrate is most stable in 73% ( $D^{15}$  1.435) or a weaker nitric acid, the next hydrate in 73—81% ( $D^{15}$  1.1435—1.1463), and the last in nitric acid stronger than 81%. **CHEMICAL ABSTRACTS.**

**Phosphomolybdic and Phosphotungstic Acids and Allied Substances.** HSEIN WU (*J. Biol. Chem.*, 1920, **43**, 189—220).—The somewhat confused literature on these acids is reviewed. There are two series of these complex acids, in which the ratios  $\text{P}_2\text{O}_5:\text{XO}_3$  are 1:18 and 1:24 respectively, and simple methods for their preparation are given.

There appear to be two isomeric forms of the phosphotungstic acid,  $\text{P}_2\text{O}_5, 18\text{WO}_3$ , and there are a number of complex acids containing both molybdenum and tungsten which belong to both the 18- and the 24-series.

On moderate reduction, the complex acids give rise to a number of new complex acids containing lower oxides of molybdenum and tungsten. The value of the complex acids of phosphorus and tungsten or molybdenum as analytical reagents is fully treated.

J. C. D.

**An Approximate Determination of the Melting-point Diagram of the System Zirconia-Silica.** E. W. WASHBURN and E. E. LIBMAN (*J. Amer. Ceram. Soc.*, 1920, **3**, 634—640).—The melting points of mixtures of zirconia and silica were determined by heating one end of a small rod, 5 cm. long and 0.3 cm. in diameter, in an oxy-acetylene flame and measuring the temperature of the droplets of fused material with an optical pyrometer. Temperature readings could be duplicated to about  $\pm 100^\circ$ . By this means, it was found that the melting point of pure zirconia is about  $2700^\circ$ , and that of natural zircon about  $2300^\circ$ . A eutectic between  $\text{ZrO}_2$  and  $\text{ZrSiO}_4$  occurs near  $2300^\circ$ . [See *J. Soc. Chem. Ind.*, 628A.] **A. B. S.**

**Metastability of Elements and Compounds as a Consequence of Enantiotropy or Monotropy. II. Antimony Tri-iodide.** ERNET COHEN and H. R. BRUINS (*Zeitsch. physikal. Chem.*, 1920, **94**, 465—470. Compare this vol., ii, 620).—Antimony iodide has been stated by Cooke (*Proc. Amer. Acad.*, 1878, **5**, 1, 72) to belong to the enantiomorphic substances, and to crystallise in red, hexagonal crystals and yellow, rhombic crystals with a transition point at  $114^\circ$ . This change has been carefully

re-examined, and it is shown that antimony iodide is a monotropic substance, and that the temperature  $114^{\circ}$  found by Cooke was accidental. Antimony iodide prepared by sublimation is a metastable system, which may remain unchanged for long periods even at low temperatures.

J. F. S.

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## Mineralogical Chemistry.

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**Regular Grouping of Two Minerals in Titaniferous Iron-ores.** A. LACROIX (*Compt. rend.*, 1920, 171, 481—485).—The compound  $\text{FeTiO}_3$  (corresponding with  $\text{TiO}_2$  52·65,  $\text{FeO}$  47·35%) is represented most nearly in nature by the mineral crichtonite from Oisans, Isère, and it is proposed to limit this name to such a compound. In most ilmenites, however, the composition is more complex, and was represented by Rammelsberg as  $\text{FeTiO}_3 + x\text{Fe}_2\text{O}_3$ . These two components have been assumed to form an isomorphous mixture (although they do not possess the same degree of symmetry) or to form a solid solution; or, again, the isomorphous mixing of  $\text{Ti}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  has been assumed. Specimens of ilmenite from Madagascar, however, show very distinctly a fine, lamellar intergrowth of two minerals (crichtonite and hæmatite) similar to the perthitic intergrowth of the feldspars. The layers of hæmatite are attacked by hydrochloric acid, leaving, finally, isolated lamellæ of crichtonite. Analysis by Raoult of a specimen from Andongovato, near Itrongay, gave:

$\text{TiO}_2$ .	$\text{FeO}$ .	$\text{MnO}$ .	$\text{MgO}$ .	$\text{Fe}_2\text{O}_3$ .	Total.	Sp. gr.
27·41	23·99	0·22	0·25	47·95	99·82	4·96

corresponding with hæmatite 47·95 and crichtonite 51·87%. The original ilmenite from the Ilmen Mtns. (containing  $\text{TiO}_2$  45—48%) appears to be homogeneous, but the washingtonite variety from Litchfield, Maine ( $\text{TiO}_2$  22—24%), shows very distinctly the perthitic intergrowth, whilst in crystals from Snarum, Norway ( $\text{TiO}_2$  6—10%), the bands of crichtonite are very thin. The name ilmenite is therefore reserved for the homogeneous types, and washingtonite for those showing the intimate intergrowth of the two minerals. Similar regular intergrowths are also shown by the titaniferous magnetites of Madagascar, the two minerals in this case being magnetite and crichtonite. Layers of needles of brown rutile enclosed parallel to the octahedral planes of the magnetite are shown to be due to the secondary transformation of crichtonite

L. J. S.

**Blödite and other Minerals of the Saliferous Stratum of Monte Sambuco in the Calascibetta Region (Sicily).** F. MILLOSEVICH (*Atti R. Accad. Lincei*, 1920, [v], 29, i, 344—347).—Crystals of blödite, some colourless and others red, owing to

inclusions of ferric oxide, occur locally in the deposit of hard salt, consisting essentially of kieserite and rock-salt, found in the saliferous mass of Monte Sambuco; they belong to the monoclinic system,  $a:b:c=1.34939:1.067047$ ,  $\beta=79^{\circ}21'42''$ . The percentage composition:

Na <sub>2</sub> O.	MgO.	SO <sub>3</sub> .	H <sub>2</sub> O.	Insol.	Total.
18.51	12.00	47.41	21.42	0.49	99.83

agrees well with the formula  $\text{Na}_2\text{SO}_4, \text{MgSO}_4, 4\text{H}_2\text{O}$ .

The name blödite has a prior claim to astracanite, which was used first to indicate the rock, that is, the material forming distinct layers in the saliferous deposits, such as those of the salt lakes of the Astracan steppe.

The astracanite mass of the upper gallery of Monte Sambuco contains many rounded, white nodules, which vary in size (peas to oranges), have a granular, saccharoid structure, deliquesce partly in moist air, contain boric acid, magnesium, and chlorine, and closely resemble the nodules of compact boracite (stassfurtite) occurring among the carnallite of the Stassfurt deposits.

T. H. P.

**Optical Properties of Anthophyllite.** N. L. BOWEN (*J. Washington Acad. Sci.*, 1920, **10**, 411—414).—A revision of the optical constants for Penfield's (1890) original material from Franklin, North Carolina (containing  $\text{SiO}_2$  57.98,  $\text{Al}_2\text{O}_3$  0.63,  $\text{FeO} + \text{MnO}$  10.70,  $\text{MgO}$  28.69%), gave:  $\alpha=1.6195$ ,  $\beta=1.6301$ ,  $\gamma=1.6404$ ,  $\gamma-\alpha=0.0209$ ,  $2V=88^{\circ}46'$  (Na). For the artificial magnesium metasilicate (kupfferite) described by Allen, Wright, and Clement (1906), revised values are:  $\alpha=1.584$ ,  $\gamma=1.597$ . In anthophyllite, the refractive indices increase regularly with the percentage of ferrous oxide.

L. J. S.

**The Existence in Madagascar of a Silicate of Scandium and Yttrium, Thortveitite.** A. LACROIX (*Compt. rend.*, 1920, **171**, 421—423).—Thortveitite has been found in the pegmatite at Befanamo, in Madagascar, and resembles in its properties the same mineral previously discovered in Iveland, Norway, and described by Schetelig (*A.*, 1912, ii, 56).

W. G.

### Analytical Chemistry.

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**Theory of Indicators Used in Acidimetry.** GUSTAV F. HÜTTIG (*Zeitsch. physikal. Chem.*, 1920, **95**, 280—284).—A theoretical paper in which the results of Wegscheider (A., 1916, ii, 108) and the previous paper of the author (A., 1914, ii, 597) are discussed, and the optical and electrochemical behaviour of indicators further developed.

J. F. S.

**A Polychromatic Indicator.** JAMES MOIR (*J. S. African Assoc. Anal. Chem.*, 1920, **3**, 6—8).—The indicator is 3:3-dihydroxybenzaurine-2-sulphonic acid, and is prepared by condensing catechol with *o*-sulphobenzoic acid. It exhibits the following range of colours in acid and alkaline solutions: strong acid, purplish-pink; dilute acid ( $N/10$ ), salmon-orange; more dilute acid ( $N/40$ ), yellow; neutral solution (or, more exactly,  $p_H=6.5$ ), practically colourless; dilute alkali ( $p_H=7.5$ ), violet; stronger alkali ( $p_H=10$ ), indigo-blue; concentrated alkali, grass-green.

W. P. S.

**Use of Potassium Hydrogen Phthalate as a Standard in Alkalimetry.** F. D. DODGE (*J. Amer. Chem. Soc.*, 1920, **42**, 1655—1656. Compare Hendrixson, this vol., ii, 382).—In the preparation of potassium hydrogen phthalate for use as a standard in alkalimetry, it is advisable to crystallise above  $20^\circ$ , because in this way the formation of a more acid salt,  $2KHC_8H_4O_4 \cdot C_8H_6O_4$ , is effectually prevented.

J. F. S.

**Influence of Atmospheric Carbon Dioxide on Alkalimetric Titrations, using Phenolphthalein as Indicator.** G. BRUHNS (*Zeitsch. Zuckerind. Čechoslav.*, 1920, **44**, 331—335).—Comparative titrations with  $N/100$ -sodium hydroxide and hydrochloric acid solutions, using phenolphthalein and methyl-orange as indicators, showed that, with the former indicator, less acid was required to neutralise a given quantity of the alkali than when methyl-orange was employed. The difference was about 0.5 c.c. per 10 c.c. of acid used, and was due to carbon dioxide absorbed from the atmosphere during the titration.

W. P. S.

**The Significance of the Dissociation Constant in the Identification of Acids and the Detection of Impurities Therein.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1920, **57**, 514—518).—The dissociation constant of weak organic acids may be used for their characterisation. This may be conveniently determined by estimating the hydrogen-ion concentration at a given dilution by comparing the colour change of the same indicator in the solution and in a standard solution of known ion concentration. Such standard solutions are represented by very dilute hydrochloric acid or by mixtures of potassium hydrogen phthalate with hydrochloric acid or sodium hydroxide. A selection of suitable indicators is given for various weak acids. The mineral acid or base in a solution of an organic acid may be estimated by measuring the change in the  $p_H$  value of the solution consequent on the addition of a known small quantity of mineral acid or base. The method of calculation is exemplified in the case of tartaric acid. W. S. M.

**The Neutralisation of Weak Acids with Weak Bases and the Examination of the Purity of Ammonium Salts of Weak Acids.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1920, **57**, 787—796).—The exact titration of a weak acid with a weak base

is practicable if a suitable indicator is chosen, the choice of the latter being determined by the hydrogen-ion concentration of the resulting salt solution; that is, the  $p_H$  value to which it is desired to titrate must be determined beforehand. An expression,

$$[H'] = \sqrt{K_{H_2O} \cdot K_{HA} / K_{BOH}},$$

is derived giving the hydrogen-ion concentration in terms of the dissociation constants of the weak acid, the weak base, and water. With the help of this equation, the  $[H']$  for mixtures of acid and base is calculated, and the neutralisation curve constructed by plotting  $p_H$  against the composition of the mixture. This curve shows an inflexion for the  $p_H$  corresponding with the neutral point. An indicator is then chosen for which the  $p_H$  in the range of colour change is approximately equal to the calculated value. For example, in the titration of ammonium acetate ( $p_H = 7.1$ ), neutral-red with a range  $p_H = 6.8$  to  $p_H = 8.0$  is chosen. Satisfactory results were obtained for ammonia and oxalic acid (neutral-red), ammonia and succinic acid (neutral-red), ammonia and formic acid (methyl-red), and ammonia and salicylic acid (methyl-red). A method for testing the purity of ammonium salts of weak acids is indicated.

W. S. M.

**Liquid Ammonia-Sodium Method for the Estimation of Halogens in Organic Compounds.** F. B. DAINS and R. Q. BREWSTER (*J. Amer. Chem. Soc.*, 1920, **42**, 1573—1579).—It has been pointed out by Clifford (A., 1919, ii, 423) that in some cases there is a considerable formation of cyanide in the estimation of halogens by the liquid ammonia-sodium process. With the object of ascertaining to what extent and in what circumstances this occurs, the reaction has been carried out with 123 organic compounds, some of which did not contain any halogen, and the resulting solutions tested for cyanide. In most cases there was no cyanide present, but in a few, such as chloroform, bromoform, chloral hydrate, and bromal hydrate, considerable quantities of sodium cyanide are formed, according to the equation  $CHBr_3 + NH_3 = HCN + 3HBr$ , whilst acetonitrile, phenylacetonitrile, and cyanoacetic ester also yield cyanide by direct separation. Cyanides are also formed by ethylidene chloride, tetrachloroethylene, and tetrachloroethane. In all these cases, the estimation of the halogen can be carried out by the modification of the method put forward by Clifford (*loc. cit.*). A large number of estimations are recorded which show that this method of analysis is trustworthy. Attempts to use the liquid ammonia-sodium method for the estimation of cyanogen in organic compounds have shown the unsuitability of the process for this purpose, chiefly because of the formation of amines, according to the equation  $CH_3 \cdot CN + 4NH_3 + 4Na = C_2H_5 \cdot NH_2 + 4NaNH_2$ . It is a remarkable fact that iodoform does not give cyanide by this process.

J. F. S.

**Use of Alundum Filtering Crucibles.** D. T. ENGLIS (*J. Ind. Eng. Chem.*, 1920, **12**, 799—800).—Soluble salts may be removed from the upper part of an alundum crucible in which a

precipitate has been collected by supporting the crucible in a suitable holder in an ordinary glass funnel, covering the top of the crucible with a rubber stopper, applying suction to the stem of the funnel, and pouring the wash-water into the top of the latter.

W. P. S.

**Chemical Analysis with Membrane Filters.** L. MOSER and KITTL (*Chem. Zeit.*, 1920, **44**, 637—638).—Whilst membrane filters (A., 1918, ii, 307) are useful for the collection of colloidal precipitates, their use in quantitative analysis is limited by the fact that, in spite of the smooth surface of the filter, it is impossible to remove the whole of the precipitate for weighing, since particles of the precipitate appear to become embedded in the membrane (compare also A., 1919, ii, 520)

W. P. S.

**Wash-bottle for giving a Continuous Stream of Water.**

HANS KLEIN (*Chem. Zeit.*, 1920, **44**, 599).—The mouthpiece of an ordinary wash-bottle is fitted with a length of rubber tubing which may be closed with a spring clip, the "bow" of the clip fitting round the cork of the bottle. The bottle is used in the usual way, the clip being closed when there is a sufficient pressure in the bottle and opened to stop the flow of water from the jet.

W. P. S.

**Apparatus for Evolution Methods of Analysis.** E. R.

DOVEY (*Analyst*, 1920, **45**, 330—332).—An apparatus suitable for the estimation of available oxygen in manganese dioxide, sulphur in steel, etc., consists of a reaction flask, the delivery tube of which extends into a test-tube containing the solution for absorbing the evolved gas; the test-tube may in turn be connected with a small U-tube containing a small quantity of absorbing solution. A tube extends to the bottom of the reaction flask, and admits air when the pressure in the flask decreases from any cause. Another apparatus, which may be used for absorbing carbon dioxide in the estimation of carbon in steel by the wet combustion method, consists of a reaction flask fitted with a reflux apparatus; the long stem of a tapped funnel extends through the inner tube of the reflux apparatus to the bottom of the flask. The carbon dioxide is conducted from the top of the reflux apparatus to the bottom of a burette containing barium hydroxide solution and in which a rod fitted with discs is placed (an efficient absorption apparatus). The top of the burette is connected with an aspirator. When the absorption of the carbon dioxide is complete, the jet of the burette is passed through a rubber stopper closing a filter tube, the contents of the burette are filtered, and the barium carbonate washed.

W. P. S.

**The Calibration, Accuracy, and Use of Gas Meters.**

AUGUST KROGH (*Biochem. J.*, 1920, **14**, 282—289).—A large recording spirometer for calibrating gas meters is described. When properly handled, wet gas meters are instruments of precision. Motor-driven wet meters acting as pumps and having a constant

water level maintained by a slow current of water are accurate to less than 0.1% at all rates below 1 revolution per minute. When calibrated for more rapid rates, they can be used with almost the same accuracy at rates up to 3 revolutions per minute. The volume per revolution decreases with increasing rate. In wet meters with a constant quantity of water the volume per revolution increases with increasing rate, but can be determined with equal accuracy.

Dry gas meters are on the whole less accurate than wet meters, and when arranged to show the volumes directly in litres their indications are often very inaccurate and cannot be calibrated. They should be arranged to count revolutions. Gas volumes representing fractions of a complete revolution are generally very inaccurately indicated, but the volume corresponding with a whole revolution is a practically constant quantity. Varying rates may cause variations in the volume registered, but at practicable rates the variation is usually within 1%. The calibration of a dry meter changes with age.

J. C. D.

**Estimation of Iodine in Connexion with Studies in Thyroid Activity.** III. E. C. KENDALL [with AVRINA PUGH, F. S. RICHARDSON and C. FORRES] (*J. Biol. Chem.*, 1920, **43**, 149—159).—The method previously described (A., 1912, ii, 864; 1914, ii, 815) is modified to render it applicable to the estimation of iodine in blood and tissue. The modifications consist mainly of the removal of oxidising substances from the phosphoric acid employed by reduction with aluminium, the adjustment of the acidity during boiling, and the use of a small piece of hard coal to facilitate the removal of the added bromine.

J. C. D.

**Estimation of Iodine in Blood and in Animal Tissues.** IV. E. C. KENDALL and F. S. RICHARDSON (*J. Biol. Chem.*, 1920, **43**, 161—170).—The application of the method described in the previous paper, to the analysis of tissues poor in iodine, such as blood, was not practicable until a method of destroying large amounts of organic matter without loss of iodine had been evolved. Destructive distillation of the tissue with about 3% by weight of sodium hydroxide at 300—400° destroys much of the organic matter without appreciable loss of iodine. The charred residue is then extracted with water, and much of the residual organic matter in the brown solution is removed by treatment with barium hydroxide. A second fusion in a small crucible, after evaporation to dryness, effects complete incineration. Special forms of heating chambers for the crucibles are described.

J. C. D.

**Volumetric Estimation of Hydrosulphides in the Presence of Sulphides, Thiosulphates, and Sulphites.** A. WÖBER (*Chem. Zeit.*, 1920, **44**, 601).—Sodium hydrosulphide when treated with excess of mercuric chloride solution yields free hydrochloric acid according to the equation  $2\text{NaHS} + 3\text{HgCl}_2 = 2\text{NaCl} + \text{Hg}_3\text{S}_2\text{Cl}_2 + 2\text{HCl}$ ; under similar conditions sodium thiosulphate gives

free sulphuric acid (compare Sander, A., 1916, ii, 111), whilst sodium sulphide gives a neutral solution. By titrating the acidity produced by mercuric chloride before and after the test solution has been treated with zinc carbonate, the quantities of thiosulphate and hydrogen sulphide may be estimated; the other constituents may be estimated as described by Sander (*loc. cit.*). W. P. S.

**Estimation of Selenium [in Organic Compounds].** FRITZ WREDE (*Zeitsch. physiol. Chem.*, 1920, 109, 272—275).—The method here described is based on that given by Pregl for the estimation of sulphuric acid ("Die quantitative organische Mikroanalyse," 1917, 122), and consists in burning the substance in a tube in oxygen in presence of platinum as catalyst and titrating the selenious acid formed with centinormal sodium hydroxide solution, sodium hydrogen selenite being neutral to methyl-orange. [See also *J. Soc. Chem. Ind.*, 1920, October.] T. H. P.

**Estimation of Ammonia in Urine [with Remarks on the Technique of the Micro-Kjeldahl Method].** LUDWIG PINCUSOHN (*Biochem. Zeitsch.*, 1919, 99, 267—276).—The urine is heated in the distilling flask of a modified micro-Kjeldahl apparatus at 45° with sodium carbonate, and the ammonia is aspirated into a receiver containing standard sulphuric acid and is estimated either by titration or colorimetrically. The time taken for the distillation of the ammonia (ten minutes) is not sufficiently long to allow the conversion of the urea into ammonia. S. S. Z.

**Estimation of Phosphorus in Small Quantities of Blood and Blood-serum.** POUL IVERSEN (*Biochem. Zeitsch.*, 1920, 104, 22—29).—The author describes a modification of Neumann's method (A., 1903, ii, 243), which admits of the estimation of phosphorus in small volumes of blood or serum (compare Feigl, A., 1919, i, 138). T. H. P.

**Titrimetric Estimation of Phosphoric Acid by Neumann's Method.** POUL IVERSEN (*Biochem. Zeitsch.*, 1920, 104, 15—21).—In this method for estimating phosphorus in organic substrata (A., 1903, ii, 243), the organic matter is destroyed by means of sulphuric and nitric acids, the phosphate formed precipitated as ammonium phosphomolybdate, and the latter washed with ice-cold water, which is filtered; the filter and precipitate are then treated with slightly more  $N/2$ -sodium hydroxide solution than is necessary to dissolve the precipitate, and the ammonia thus liberated boiled off and estimated by titration:  $(\text{c.c. of } N/2\text{-NaOH}) \times 0.5539 = \text{amount of phosphorus in milligrams}$ . Gregersen (A., 1908, ii, 64) found it to be necessary to over-titrate with 0.5—1 c.c. of acid and to boil to expel carbon dioxide. Heubner (A., 1914, ii, 675), who dissolves the precipitate on the filter by means of the standard sodium hydroxide solution, gives, however, a higher factor than the above, namely, 0.57. The author shows that Gregersen's



modification gives good results, provided that the excess of  $N/2$ -NaOH taken is at most 4 c.c., and is subject to no systematic error; the mean value of the factor is found, from twenty-five analyses, to be 0.5526 (compare Kleinmann, this vol., ii, 634).

T. H. P.

**Estimation of Phosphoric Acid in Phosphates of the Heavy Metals.** F. SEBLIGMANN (*Chem. Zeit.*, 1920, 44, 599).—The phosphate (10 grams) is heated at 90–95° for fifteen minutes with 12 grams of sodium hydroxide solution (D 1.383), the mixture diluted with 4 parts of water, boiled, cooled, diluted to 1 litre, filtered, and an aliquot portion of the filtrate acidified with acetic acid and titrated with uranyl acetate solution. W. P. S.

**Estimation of Phosphoric Acid. I. (1) The Estimation of Phosphoric Acid as Magnesium Ammonium Phosphate and the Hindrance of its Precipitation by the Serum Constituents. (2) The Estimation of Phosphoric Acid as Uranium Phosphate and as Silver Phosphate.** HANS KLEINMANN (*Biochem. Zeitsch.*, 1919, 99, 19–45).—Serum constituents, such as potassium dihydrogen phosphate, urea, glycine, or calcium carbonate, do not influence the precipitation of phosphoric acid as magnesium ammonium phosphate. The presence of sodium chloride in certain concentrations, on the other hand, leads to high results. Reagents, such as picric acid and trichloroacetic acid, employed in the precipitation of proteins influence the precipitation, although they do not hinder it. Serum does not contain any substances which are capable of preventing the complete precipitation of phosphoric acid as magnesium ammonium phosphate. On precipitating 1 mg. of  $P_2O_5$  as magnesium ammonium phosphate in 50–75 c.c. of solution, 0.006 mg. remains unprecipitated. With a smaller quantity (0.1 mg.) of  $P_2O_5$  the unprecipitated fraction is even proportionately higher. The uranium acetate method yields good results with quantities as low as 10 mg. of  $P_2O_5$ . Quantities below 10 mg. give untrustworthy results. With Liebermann's silver phosphate method high results are obtained, whilst the estimation of phosphoric acid as the vanadium-phosphoric acid-molybdenum complex is found satisfactory. Columbium and tantalum produce no specific coloration with phosphoric acid and molybdenum. S. S. Z.

**Estimation of Phosphoric Acid. II. The Estimation of Phosphoric Acid in Phosphomolybdates. Gravimetric and Colorimetric Methods.** HANS KLEINMANN (*Biochem. Zeitsch.*, 1919, 99, 45–95).—The precipitation of molybdenum by Raper's method gives too high values. Preliminary colorimetric experiments have shown that the coloured compounds produced by molybdenum with tannin or the phenols are entirely unsuitable for quantitative analysis. The phenylhydrazine compounds yield untrustworthy results, but the molybdenum-red reaction (potassium thiocyanate) is satisfactory. The most suitable results are obtained with potass-

ium ferrocyanide. One mg. of molybdenum was estimated in 100 c.c. with an error of 0.5%. The procedure was successfully applied for the colorimetric estimation of phosphoric acid, which was precipitated as phosphomolybdate and the molybdenum then estimated colorimetrically with potassium ferrocyanide; 0.1 mg. of  $P_2O_5$  can be estimated by this method with an error of 0.5%. An attempt to devise a satisfactory method for the estimation of ammonium in the phosphoric acid molybdenum complex failed. S. S. Z.

**Estimation of Phosphoric Acid. III. The Estimation of Phosphoric Acid in Phosphomolybdates. Volumetric and Sedimetric Methods.** HANS KLEINMANN (*Biochem. Zeitsch.*, 1919, **99**, 95—115).—Low results were obtained with Neumann's method for the estimation of phosphorus when the theoretical factor was used. By washing the ammonium phosphomolybdate precipitate with 50% alcohol instead of water, better results were obtained. In micro-Neumann estimations it is more satisfactory to wash the precipitate than to centrifuge it, as a certain amount of loss is thus obviated. The author describes a "sedimetric" method by means of which the phosphorus is rapidly estimated by measuring the volume of the precipitate after centrifuging it in a graduated tube. The height of the ammonium phosphomolybdate precipitate is proportional to its  $P_2O_5$ -content. S. S. Z.

**Estimation of Phosphoric Acid. IV. The Estimation of Phosphoric Acid as a Strychnine-Phosphoric Acid-Molybdenum Compound (Nephelometry). The General Principles of Nephelometry and the Construction of a New Nephelometer.** HANS KLEINMANN (*Biochem. Zeitsch.*, 1919, **99**, 115—150).—A description of the development of nephelometry. A new nephelometer and its manipulation are also described. S. S. Z.

**Estimation of Phosphoric Acid. V. The Estimation of Phosphoric Acid as a Strychnine-Phosphoric Acid-Molybdenum Compound. Special Phosphoric Acid Nephelometry and a New Method of Preparation of the Strychnine-Molybdenum Reagent.** HANS KLEINMANN (*Biochem. Zeitsch.*, 1919, **99**, 150—190).—Strychnine sulphate and sodium molybdate react in moderately concentrated hydrochloric acid solution to form a clear, colourless, stable reagent, which is suitable for the estimation of phosphoric acid; 0.1—0.0005 mg. of  $P_2O_5$  can be estimated in this way by a nephelometric method with an error of 0.5%. S. S. Z.

**Estimation of Minute Quantities of Arsenic by Titration.** H. H. GREEN (*J. S. African Assoc. Anal. Chem.*, 1920, **3**, 3—4).—For quantities of arsenic trioxide ranging from 0.05 to 5 mg., the solution containing the arsenic is treated as usual in a Marsh apparatus and the evolved gases are passed successively through a vessel

containing lead acetate solution and three vessels containing dilute silver nitrate solution. The contents of the silver nitrate vessels are then mixed, treated with sodium hydrogen carbonate, solid potassium iodide is added until the precipitated silver iodide has re-dissolved, and the mixture is titrated with *N*/500-iodine solution. Each c.c. of the latter is practically equivalent to 0.1 mg. of arsenic trioxide. The black silver precipitate need not be removed before the titration is made.

W. P. S.

**Electrometric Analysis of Arsenicals.** CHARLES S. ROBINSON and O. B. WINTER (*J. Ind. Eng. Chem.*, 1920, **12**, 775—778).—The electrometric apparatus used is essentially that described by Hillebrand (A., 1913, ii, 721), except that a mechanical stirrer is added and a reflecting galvanometer of the box type employed in place of the capillary electrometer. The titration of arsenic trioxide is made with iodine solution in the presence of sodium hydrogen carbonate, whilst arsenic pentoxide is titrated at 95° in 50% sulphuric acid solution with sodium iodide solution. The method is particularly suitable for the estimation of arsenic in coloured solutions.

W. P. S.

**Estimation of Carbon Dioxide in Carbonates Insoluble in Water.** C. S. ROBINSON (*Soil Sci.*, 1920, **10**, 41—47).—Estimations were made of the carbonate content of samples of limestone, marl, and soil. The first method used was that of Van Slyke (A., 1919, ii, 78). The second method was a gasometric one, originally proposed for soluble carbonates by Van Slyke (A., 1917, ii, 422). A special form of cup nitrometer was used, with a tube and special stopper holding the weighed sample introduced between the end of the nitrometer and the levelling tube, which contained mercury. The apparatus having been freed from air, hydrochloric acid was introduced from the cup. After all the gas was evolved, its volume was measured and its weight calculated from tables prepared for the conditions of the determination. The gasometric method was the more accurate of the two, but the first method was to be preferred for samples low in magnesium carbonate.

J. H. J.

**Micro-method for the Estimation of the Carbon Dioxide of the Blood.** A. KROGH and G. LILJESTRAND (*Biochem. Zeitsch.*, 1920, **104**, 300—315).—Various modifications are introduced into Barcroft and Haldane's method for estimating the carbon dioxide of the blood (A., 1902, ii, 424); 0.25—0.3 c.c. of blood suffices for two estimations, the mean error of the result being  $\pm 0.5\%$  by volume.

T. H. P.

**Estimation of Potassium and Sodium Present Together.** A. QUARTAROLI (*Gazzetta*, 1920, **50**, ii, 64—69).—The disadvantages of the ordinary methods for estimating separately potassium and sodium may be overcome by converting the weighed mixture of the chlorides into nitrates and determining the melting

point of the mixed nitrates, first alone, and, secondly, after admixture with an equal weight of pure potassium nitrate; the melting-point curve falls sharply from  $336^{\circ}$  ( $\text{KNO}_3$ ) to  $220^{\circ}$  (about 55%  $\text{KNO}_3$ ), and then rises sharply to  $306^{\circ}$  ( $\text{NaNO}_3$ ). If  $P$  represents the weight of the mixed chlorides and  $a$  the percentage of potassium nitrate in the mixed nitrates, as indicated by the melting point, then the weight of potassium chloride in the weight  $P$  of mixed chlorides will be given by  $x = 1.0723aP / (0.0723a + 100)$ . [See also *J. Soc. Chem. Ind.*, 1920, October.] T. H. P.

**Estimation of Total Calcium in Soils and the Significance of this Element in Soil Fertility.** O. M. SHEDD (*Soil Sci.*, 1920, 10, 1—14).—A more rapid and accurate method than that already in use for the estimation of calcium in soils, and one in which the production of an ammonia precipitate, which occludes calcium, is avoided, is described. One gram of the sample is fused with fusion mixture and the silica separated in the usual manner. The filtrate is made just alkaline with ammonia, and then just acid with hydrochloric acid, heated to the b. p., and precipitated with 1—2 grams of solid ammonium oxalate. The mixture is kept on the steam-oven for a few hours, and then at the ordinary temperature overnight. The precipitate is filtered and ignited. The oxide or carbonate is dissolved in hot dilute hydrochloric acid, and bromine water and ammonia added to precipitate manganese. The solution is acidified with acetic acid, and the manganese filtered off. The filtrate is then reprecipitated as before.

Analyses by this method of a large number of soils, both cultivated and uncultivated, showed that cultivation led to a considerable loss of calcium. The more fertile soils contained the most calcium. The application to soils poor in calcium of limestone or rock phosphate is beneficial, on account of the calcium they supply as plant food, apart from any other benefit they confer.

J. H. J.

**Estimation of Calcium in Small Quantities of Blood Serum.** BENJAMIN KRAMER and JOHN HOWLAND (*J. Biol. Chem.*, 1920, 43, 35—42).—One or 2 c.c. of serum are evaporated to dryness in a platinum crucible and gently incinerated. The ash is dissolved in a small quantity of  $N$ -hydrochloric acid, and the solution again evaporated to dryness and incinerated. The crystalline residue is readily soluble in not more than 1 c.c. of  $0.1N$ -sulphuric acid, and this solution is quantitatively transferred to a special type of 2 c.c. calibrated tube. After neutralisation by ammonia and warming, the calcium is precipitated by an excess (0.3 c.c.) of  $0.1N$ -oxalic acid in  $0.05N$ -sulphuric acid. The reaction must be acid at this point. Heating is continued for a few minutes, 0.1 c.c. of a saturated solution of sodium acetate is added, the tube is well shaken, and the volume is made up to 2.0 c.c. After several hours, the precipitate is filtered through a hardened filter, and the excess of oxalic acid in 1 c.c. of the filtrate is estimated by titration with  $0.01N$ -potassium permanganate. A

blank estimation on the reagents is necessary. The method appears to be trustworthy.

The results previously reported by Howland and Marriott (A., 1918, ii, 21) on the calcium of the serum in infantile tetany are confirmed. J. C. D.

**Use of Organic Solvents in the Quantitative Separation of Metals. III. Separation of Magnesium from Sodium and Potassium Chlorides.** S. PALKIN (*J. Amer. Chem. Soc.*, 1920, 42, 1618—1621. Compare A., 1917, ii, 43).—The method previously published for the separation of lithium from sodium and potassium (*loc. cit.*) has been modified and adapted to the separation of magnesium from sodium and potassium. The modified method depends on a progressive precipitation of the sodium and potassium chlorides from a concentrated solution by the use of alcohol and ether, and is divided into two stages: (i) in which all but a few milligrams is precipitated, and (ii) in which the last few milligrams are removed from solution. The estimation is carried out as follows: the total chlorides of magnesium, sodium, and potassium are dissolved in the minimum quantity of water (about 1.5 c.c. of water are sufficient for 0.5 gram of substance), one drop of concentrated hydrochloric acid is added, and gradually 25 c.c. of absolute alcohol are dropped into the liquid while rotating. The sodium and potassium chlorides should precipitate in a uniform granular condition. In a similar manner, 25 c.c. of ether are added, and the mixture is kept until the precipitate is agglomerated and the supernatant liquid nearly clear. The mixture is filtered, and the beaker and precipitate are washed with a mixture of one part of alcohol and four parts of ether. The filtrate is evaporated to dryness on a steam-bath; the residue is dissolved in 10 c.c. of alcohol, one drop of concentrated hydrochloric acid added, and the mixture warmed until practically everything has dissolved. The beaker is then rotated and 50 c.c. of ether slowly added, and the mixture kept for twenty minutes. The precipitate is collected on the same filter, washed with the ether-alcohol mixture, dried, ignited, and weighed. The filtrate containing the magnesium is evaporated nearly to dryness, dissolved in 5—10 c.c. of concentrated hydrochloric acid and a little water, sodium hydrogen phosphate is added, and the estimation completed in the usual way. The method has several advantages over the usual method, namely, (i) it affords a direct estimation of the sodium and potassium salts, inasmuch as they are precipitated first rather than after the magnesium, (ii) the reagents used are volatile organic solvents, and (iii) no foreign salt or base is introduced as a precipitating agent. J. F. S.

**Magnesia Mixture.** O. KUHN (Chem. Zeit., 1920, 20, 586).—If "magnesia mixture" is prepared without the addition of ammonia, it may be kept for an indefinite period in glass bottles without the glass being attacked, with the consequent formation of a precipitate in the reagent. The absence of ammonia does not

interfere with the use of the reagent for the precipitation of phosphoric acid; only a slight excess of the reagent should be employed, and ammonia added subsequently in sufficient quantity.

W. P. S.

**Estimation of Small Amounts of Copper by the Iodide Method.** H. F. BRADLEY (*J. Ind. Eng. Chem.*, 1920, **12**, 800).—

The precipitate of cupric sulphide is washed, moistened with a few drops of concentrated zinc nitrate solution, and ignited. The residue of oxides is dissolved in dilute hydrochloric acid (1:1), the solution neutralised with 5% potassium hydroxide solution, acidified with acetic acid, a small amount of phosphate solution is added, followed by 2 grams of sodium iodide, and the liberated iodine is titrated.

W. P. S.

**Estimation of Mercury in Urine.** R. FABRE (*J. Pharm. Chim.*, 1920, [vii], **22**, 81—85).—One litre of the urine is heated under a reflux apparatus with 100 c.c. of hydrochloric acid, and 6 grams of potassium chlorate are added in small quantities at a time during a period of about two hours. The solution is boiled under the reflux apparatus to expel the greater part of the free chlorine, cooled, treated with sulphur dioxide, and again boiled. After filtration, the solution is treated with 15 c.c. of stannous chloride solution, heated for two hours on a water-bath, and at the end of twenty-four hours the liquid is decanted from the grey precipitate. The latter is treated with a few c.c. of hydrochloric acid to cause the mercury to collect in a globule, which is washed with water, alcohol, and ether, dried over sulphuric acid, and weighed. If the quantity of mercury is very small, it may be collected on a gold-coated asbestos filter, as recommended by Farup.

W. P. S.

**Some Microchemical Methods.** ALFRED BRAMMALL (*Geol. Mag.*, 1920, **57**, 123—125).—The following microchemical tests for iron and manganese are described. (1) *Detection of iron*: The cover glass is removed, and the slide is cleansed of balsam, polished, again cleansed, and warmed. Reaction paper is prepared by soaking pieces of white drawing paper in concentrated hydrochloric acid and pressing them in similar sheets until no longer wet. An ammonium thiocyanate paper is similarly prepared. The acid paper is carefully laid on the section, covered with a strip of cardboard on which is laid a hot iron for two or three minutes. After the slide has dried, the thiocyanate paper is similarly applied, pressed in the cold, and again dried. The distribution of ferric iron is revealed by a transparent blood-red stain of ferric thiocyanate. Potassium ferrocyanide similarly used gives an opaque blue coloration which must be examined in reflected light. The method was found valuable in the examination of the "spotted rocks" of Andlauthal, Vosges; of dark inclusions in, and alterations of chiastolite; lamination in shales; identification of magnetite, siderite, etc. (2) *The fusion test for manganese* may be applied to slides as follows: A slide is ground down

and one side polished. The slide is then detached from the glass slip, and cleansed from balsam and dried. It is allowed to soak for several minutes in a hot saturated solution of potassium carbonate and nitrate and dried. A thin wash of the solution is applied to the polished surface and allowed to dry. This surface is subjected to the f. p. tip of the blowpipe flame for a few minutes, and after cooling is slightly polished to level the veneer of the fusion. After remounting on the slide with the prepared surface downward, the section is ground thin and examined by transmitted light. (3) *Obscure bedding planes and minute structures in chalk and limestone* may be revealed by differential solution of ground and polished sections in a bath of carbonated waters, a method approximating to weathering.

CHEMICAL ABSTRACTS.

**The Adsorption of Copper Oxide and Nickel Oxide by Precipitates of Ferric Oxide.** ER. TOPORESCU (*Compt. rend.*, 1920, **171**, 303—305).—By the addition of ammonium hydroxide to a solution of a ferric salt containing in addition either a copper salt or a nickel salt a certain amount of copper oxide or nickel oxide is always adsorbed by the ferric hydroxide, the amount depending on the relative proportions of the two salts present and the amount of ammonium hydroxide added. These oxides cannot be removed from the ferric oxide by washing the precipitate or by treatment with concentrated ammonia solution.

W. G.

**Analysis of Zirconium Minerals.** H. V. THOMPSON (*Pottery Gaz.*, 1920, **45**, 767).—In the analysis of zirconium ores two main difficulties are encountered: (1) raw zirconium ores and products manufactured therefrom are not easily decomposed, and (2) the separation of aluminium from zirconium is not readily effected. Use is made of the fact that after fusion with sodium peroxide and decomposition of the fusion with water, the residue contains all the iron, titanium, and zirconium in the form of oxides together with some of the silica, whilst the whole of the aluminium and the remainder of the silica are contained in the filtrate. This process possesses the advantage that zirconium and aluminium are automatically separated during the decomposition of the sample.

CHEMICAL ABSTRACTS.

**Differential Analysis of Acetone, Acetaldehyde, and Formaldehyde in Organic Liquids.** EMILIO PITTARELLI (*Arch. farm. Sper. sci. Aff.*, 1920, **29**, 70—87).—The various methods, depending on precipitation, coloration, or odour, for the detection of acetone, acetaldehyde, and formaldehyde are described and discussed as regards their application to fermented liquids, milk, urine, etc. In the examination of urine, the free acetone may be separated by treatment with excess of Nessler's reagent, and the combined acetone by distilling the filtrate with an acid. T. H. P.

**Colour Reaction of Milk in Presence of Formaldehyde.** ARTURO ROSSI (*Boll. Chim. Farm.*, 1920, **59**, 265—268).—The pres-

ence of formaldehyde in milk may be detected by adding 2—2.5 c.c. of the milk carefully to 2 c.c. of sulphuric acid (D 1.820—1.825) in a test-tube, so that the liquids mix as little as possible, and then shaking the tube rapidly; the liquid assumes a more or less intense violet colour, according to the proportion of formaldehyde present. The best conditions for the reaction vary with such proportion, the sensitiveness diminishing with more than 0.0005% of the aldehyde; in doubtful cases the samples to be tested may be diluted with pure milk. Other substances may be examined for formaldehyde by subjecting them to distillation, mixing part of the distillate with pure milk, and applying the sulphuric acid reaction. Milk free from formaldehyde sometimes gives this violet coloration, but only after being in contact with the sulphuric acid for some hours. T. H. P.

#### **Estimation of Minute Amounts of Acetone by Titration.**

ROGER S. HUBBARD (*J. Biol. Chem.*, 1920, **43**, 43—56).—A modification of the Messinger titration method suitable for dilute solutions of acetone. The conditions necessary for an accurate estimation have been carefully worked out and are fully described.

A method of successive distillation from acid, alkaline, and oxidising solutions is described, whereby acetone may be separated from much larger amounts of alcohol and other interfering substances.

J. C. D.

#### **Estimation of Acetone in Expired Air.**

ROGER S. HUBBARD (*J. Biol. Chem.*, 1920, **43**, 57—65).—The patient breathed for five or ten minutes through a mask or through a mouthpiece, the expired air passing through two bottles containing 75 c.c. of a freshly prepared 2.5% solution of sodium hydrogen sulphite. For the removal of interfering substances the contents of the bottles were distilled successively with 10% sodium hydroxide solution, acidified potassium permanganate solution, and a solution of sodium peroxide. In the final distillate, acetone is estimated either by the method described above (preceding abstract) or by the turbidity method, using the Scott-Wilson reagent.

J. C. D.

#### **Determination of Micro-reduction.**

D. G. COHEN TERVAERT (*Zeitsch. physiol. Chem.*, 1920, **110**, 41—54).—The experiments here described show that Bang's modified method for the micro-estimation of sugar in blood (A., 1918, ii, 278, 279; this vol., ii, 199; compare also Maclean, A., 1916, i, 613; 1919, ii, 434) is applicable only when the liquid is heated for a definite time.

The author describes a simple method, consisting in oxidation by means of chromic acid, which allows of the estimation of dextrose, lactose, and maltose. As measured by this method, the reduction of the blood is higher than is indicated by the ordinary copper methods. Dextrose added to blood is estimated quantitatively by this method.

T. H. P.

#### **Micro-estimation of Dextrose by Bang's Method.**

BERTHOLD OPPLER (*Zeitsch. physiol. Chem.*, 1920, **109**, 57—64).—The author has tested this method (this vol., ii, 199) with quantities



of pure dextrose varying from 0.545 mg. to 0.027 mg., the ratio between the weight of dextrose (mg.) and the number of c.c. of 0.01*N*-iodate solution increasing from 1:2.78 to 1:1.19, whereas Bang and Hatlehoel (A., 1918, ii, 279) gave the constant value 1:2.8 for this ratio. No greater constancy of this ratio is achieved by the use of steam for boiling the solution. Hence, for the estimation of dextrose in the blood an empirical table is necessary. It is questionable if Bang's method really suffices for the estimation of sugar in a few drops of blood, and for the estimation of 1 mg. or less of dextrose, Bertrand's method is recommended. T. H. P.

**Estimation of Minimal Quantities of Dextrose, specially in Blood.** H. C. HAGEDORN and B. NORMAN JENSEN (*Ugeskrift for Læger*, 1918, 80, 1217—1228).—The method, which gives concordant results, depends on the precipitation of proteins by zinc hydroxide, the reduction of potassium ferricyanide by dextrose, and the iodometric estimation of the excess of ferricyanide. Blood, 0.1 c.c., is added to a mixture of 5 c.c. of 0.45% hydrated zinc sulphate solution and 1 c.c. of *N*/10-sodium hydroxide, the mixture is heated in a boiling water-bath for four minutes, cooled, and filtered; the tube, precipitate, and filter are washed thrice with 3 c.c. of water. Two c.c. of a solution (1.649 grams of potassium ferricyanide and 28.6 grams of sodium carbonate decahydrate in one litre, which will keep in the dark for at least two months) are added and the mixture is heated in a boiling water-bath for fifteen minutes. After cooling, 3 c.c. of a solution (5 grams of potassium iodide, 10 grams of hydrated zinc sulphate, and 50 grams of sodium chloride in 200 c.c.) and 2 c.c. of 3% acetic acid are added, and the mixture is titrated with thiosulphate (1.24 grams of hydrated sodium thiosulphate in one litre, which must be standardised against potassium ferricyanide or 0.005*N*-potassium iodate). The difference between 2 c.c. and the volume of thiosulphate used is the volume of ferricyanide reduced by dextrose, the amount of which is determined by the following figures, in which the volume of ferricyanide in c.c. is followed by the amount of dextrose in mg.: 0.10, 0.017; 0.20, 0.035; 0.30, 0.053; 0.40, 0.070; 0.50, 0.088; 0.60, 0.106; 0.70, 0.124; 0.80, 0.141; 0.90, 0.159; 1.00, 0.177; 1.10, 0.195; 1.20, 0.214; 1.30, 0.232; 1.40, 0.251; 1.50, 0.270; 1.60, 0.290; 1.70, 0.310; 1.80, 0.331; 1.90, 0.355; 2.00, 0.384.

#### CHEMICAL ABSTRACTS.

**Improved Method for the Detection of Sugar, particularly in Urine.** WALTER S. HAINES, GILBERT P. POND, and RALPH W. WEBSTER (*J. Amer. Med. Assoc.*, 74, 301—302; from *Chem. Zentr.*, 1920, iv, 240—241).—A modified Haines solution is recommended, for which copper sulphate (5 grams), glycerol (250 c.c.), potassium hydroxide (20 grams), or sodium hydroxide (14.3 grams) are dissolved in 1 litre with distilled water. The copper sulphate is dissolved in a warm mixture of water (250 c.c.) and glycerol (250 c.c.); the alkali is dissolved separately in water

(200 c.c.), after which the solutions are mixed and made up to 1000 c.c. Five c.c. of the solution are heated to boiling and treated in an inclined test-tube with 10—20 drops of urine, the phosphate of which has been precipitated and filtered after addition of 5—6 drops of sodium hydroxide solution (5—10%). A red or yellow ring is immediately formed at the junction of the solution and urine if the latter contains more than 0.1% of sugar; if only 0.03% is present, the ring only appears after a few seconds, but, at any rate, within a minute. Smaller amounts of sugar, which then lie within physiological limits, cannot be detected, so that a positive result of the test indicates a pathological condition. H. W.

**Iodometric Estimation of the Phenyl Derivatives of Arsenious Acid.** PAUL FLEURY (*Bull. Soc. chim.*, 1920, [iv], 27, 699—704).—In continuation of previous work (this vol., i, 578) a method has been devised for estimating arsenic trichloride, phenyldichloroarsine, diphenylchloroarsine, and triphenylarsine in a mixture of the four compounds.

A benzene solution of the mixture is extracted with aqueous sodium hydroxide, whereby arsenious acid and phenylarsenious acid are extracted. This extract is acidified with hydrochloric acid until its acidity is approximately  $N/10$ , alcohol is added in equal volume, and the mixture is titrated with standard iodine solution. The iodine used is equivalent to the phenyldichloroarsine present in the original mixture. An excess of sodium hydrogen carbonate is added, and the titration is again completed. The further amount of iodine required is equivalent to the arsenic trichloride originally present. The benzene solution left after the extraction with alkali is titrated with standard iodine solution, the amount required being equivalent to the diphenylchloroarsine and triphenylarsine originally present. To the product from this titration an excess of aqueous sodium hydrogen carbonate is added, and the whole is extracted with chloroform. The chloroform extract contains triphenylarsine oxide, and if the aqueous solution is now acidified and again extracted with chloroform, the second extract will contain diphenylarsenic acid, which may be obtained in a crystalline form on evaporation of the solvent. W. G.

**Estimation of Volatile Acids in Fermentation Products.** G. HINARD (*Ann. Chim. Analyt.*, 1920, [ii], 2, 239—242).—Fifty c.c. of the liquid are mixed with 10 c.c. of water and distilled, 50 c.c. of distillate being collected and titrated. Fifty c.c. of water are then added to the contents of the distillation flask, and a second quantity of 50 c.c. is distilled and titrated. These operations are repeated several times and a curve plotted from the results; the asymptote of this curve indicates the amount of alkali solution required to neutralise the total volatile acids present. W. P. S.

**Isolation of Formic, Acetic, and Lactic Acids.** ISENOBUKE ONODERA (*Ber. Ohara Inst. landw. Forsch.*, 1917, i, 231—259; from *Chem. Zentr.*, 1920, iv, 271).—The three acids are extracted from

the mixed solution by means of ether. In one portion of the ethereal solution formic acid is titrated with permanganate, and, in this oxidised portion, the lactic acid is estimated as oxalic acid. Acetic acid is removed from the decomposed solution by means of ether, and the extract is again distilled. The method is trustworthy, and its accuracy is not influenced by the presence of small amounts of propionic and butyric acids.

H. W.

**The Colorimetric Estimation of Tyrosine by the Method of Folin and Denis.** ROSS AIKEN GORTNER and GEORGE E. HOLM (*J. Amer. Chem. Soc.*, 1920, **42**, 1678—1692).—Tyrosine cannot be estimated quantitatively in the products of protein hydrolysis by means of the phenol reagent of Folin and Denis (*A.*, 1912, ii, 1012). Tryptophan, if present, will give an intense colour with the reagent, and indole and indole derivatives, as well as ferrous salts, also give the blue colour. It seems probable that other products of protein hydrolysis may also produce blue colours with the phenol reagent. Further, in the case of tyrosine itself the depth of colour varies with the relative proportion of reagent and tyrosine present, the colour values falling off sharply as the concentration of the tyrosine increases. Protein hydrolysates must not be decolorised with carbon or bone charcoal if they are to be used subsequently for the estimation of amino-acid content, as tyrosine, tryptophan, and its decomposition products are adsorbed in appreciable amounts by bone-black. Bone-black itself contains some easily oxidisable material, which dissolves in acid solutions and then gives the blue colour with the phenol reagent.

W. G.

**Estimation of Uric Acid by Clarification of the Liquids by means of Talc.** E. LAMBLING and C. VALLÉE (*Compt. rend. Soc. Biol.*, 1920, **83**, 793—795; from *Chem. Zentr.*, 1920, iv, 217).—A portion of the uric acid is carried down by talc even from acid solutions.

H. W.

**Analytical Characters of Dichlorodiethyl Sulphide.** FELIX MARTIN (*J. Pharm. Chim.*, 1920, [vii], **22**, 161—165).— $\beta\beta'$ -Dichlorodiethyl sulphide ("mustard gas"), after oxidation, gives the usual reaction for sulphuric acid. When a small quantity of the substance is heated with alcoholic potassium hydroxide solution, and the vapours produced are passed into Denigès's reagent (an acid solution of mercuric sulphate), a white precipitate is formed; if the vapours are absorbed in water, the solution, on treatment with a drop of iodine solution, yields an odour similar to that of mercaptan. Dichlorodiethyl sulphide is hydrolysed by water, and the solution yields a turbidity when treated with Grignard and Rivat's reagent (iodine 8 grams, gum arabic solution 1 c.c., copper sulphate 0.8 gram, and water 33 c.c.).

W. P. S.

**Behaviour of Phenolphthalein with Iodine and a Method for the Estimation of Phenolphthalein.** SAMUEL PALKIN (*J. Ind. Eng. Chem.*, 1920, **12**, 766—769).—Investigation of the

action of iodine on phenolphthalein relative to the conditions governing the formation of tetraiodophenolphthalein and the physical properties of the latter, yielded information on which was based the following method for the estimation of the substance. The phenolphthalein is dissolved in 30% potassium hydroxide solution and a small quantity of water, 20 grams of ice are added, and then an excess of iodine reagent (10% of iodine in 15% potassium iodide solution, the free iodine being then combined by the addition of alkali). Concentrated hydrochloric acid is now added until precipitation is complete, more iodine is added if the liquid is not brown in colour, the precipitate is dissolved by the addition of 30% potassium hydroxide solution, and the precipitation and solution repeated three or four times. The final alkaline solution is treated with 0.5 c.c. of 10% sodium sulphite solution, acidified with hydrochloric acid, and extracted several times with acetone-chloroform mixture (1:3); the united extracts are evaporated, the residue of tetraiodophenolphthalein dried at 100°, and weighed. The weight multiplied by 0.3781 gives the amount of phenolphthalein present. W. P. S.

**Estimation of Codeine.** H. E. ANNETT and HARIDAS SEN (*Analyst*, 1920, **45**, 321—328).—The following method may be applied to opium, pure alkaloids, plant materials, etc., with suitable modification of the amounts of substance taken. Ten grams of dry opium are mixed thoroughly with 4 grams of calcium hydroxide and 100 c.c. of water, the mixture stirred for thirty minutes, filtered, and 50 c.c. of the filtrate are treated with 40 c.c. of 2% acetic acid and 10 c.c. of basic lead acetate solution (D 1.25). After filtration, 75 c.c. of the filtrate are shaken with 2 grams of calcium hydroxide for thirty minutes, the mixture filtered, and 50 c.c. of the filtrate are extracted with three successive quantities of 50 c.c. of toluene. The combined toluene extract is filtered and treated with dry hydrogen chloride, avoiding any great excess of the latter. Codeine hydrochloride separates, and, after excess of hydrogen chloride has been expelled by a current of air, is collected, dissolved in water, the solution evaporated, and the residue of codeine hydrochloride dried and weighed. W. P. S.

**Colour Tests for Nitrates and Nitrites, Antipyrine (in Pyramidone), Phenol and Aniline, and  $\alpha$ - and  $\beta$ -Naphthols.** A. ESCAICH (*J. Pharm. Chim.*, 1920, [vii], **22**, 138—141).—The author's colour test for nitrites (A., 1918, ii, 273) gives uncertain results with natural waters rich in chlorides, but the latter may first be removed by means of silver nitrate. When the nitrates of the water are to be reduced to nitrites by amalgamated aluminium, this process must precede the precipitation of chlorides. Magnesium, like aluminium, may be activated by immersion in mercuric cyanide solution and used for reducing nitrates to nitrites. A colour test is described for the detection of antipyrine in pyramidone, based on the production of violet and red colorations by conversion of antipyrine into nitrosoantipyrine, and oxidation

of the latter with lead peroxide. A very sensitive test for phenol in aqueous solutions is to treat 10—15 c.c. with five to ten drops of ammonia, 0.05—0.1 gram of sodium persulphate, and four or five drops of *N*/10-silver nitrate solution. A green coloration is produced, which changes to blue or yellow, according as the concentration of phenol was more or less than about 0.05 gram per litre.  $\alpha$ -Naphthol dissolved in aqueous alcohol and treated with sodium nitrite and a few drops of acid mercuric sulphate solution gives a fine, red coloration and red precipitate, whilst  $\beta$ -naphthol gives a yellow precipitate. J. H. L.

**Estimation of Phenol in the Presence of certain other Phenols.** ROBERT M. CHAPIN (*J. Ind. Eng. Chem.*, 1920, 12, 771—775).—The method depends on the red coloration yielded by phenol with Millon's reagent when the mixture is heated in the presence of nitric acid; most other phenols give yellow colorations, but  $\beta$ -naphthol gives a brown, and salicylic acid a red, colour. It is necessary to heat the mixture at 100° for thirty minutes in order to discharge the original red colour given by the other phenols and to allow the red colour of phenol itself to reach its full intensity. Various modifications of the method are described which are suitable for different requirements. The red coloration given by phenol may be reduced to yellow by the action of formaldehyde, whilst any yellow colour present originally is not affected. [See, further, *J. Soc. Chem. Ind.*, 1920, 652A.] W. P. S.

**Method for the Estimation of Cineole in Eucalyptus Oils.** T. TUSTING COCKING (*Pharm. J.*, 1920, 105, 81—83).—Three grams of the eucalyptus oil, dried previously over calcium chloride, are mixed with 2.1 grams of *o*-cresol, and the solidifying point of the mixture is determined. The quantity of cineole present is ascertained by reference to a graph. W. P. S.

**Estimation of Urea in Blood in Normal and Pathological Cases; Comparative Results of the Hypobromite and Xanthhydrol Methods.** M. LAUDAT (*Compt. rend. Soc. Biol.*, 1920, 83, 730—732; from *Chem. Zentr.*, 1920, iv, 68).—Considerable errors are involved in the estimation of urea in blood by the hypobromite method, since ammonia, uric acid, and creatine are decomposed by the reagent to a greater or less extent. Xanthhydrol, on the other hand, does not attack these substances. H. W.

**Estimation of Urea in Blood by Xanthhydrol.** W. MESTREZAT and MARTHE JANET (*Compt. rend. Soc. Biol.*, 1920, 83, 763—764; from *Chem. Zentr.*, 1920, iv, 217).—The experimental conditions necessary for an exact estimation have been investigated.

The xanthhydrol method is no longer exact in a 1% solution of urea; Tanret's reagent dissolves xanthylurea. The serum (10 c.c.) is diluted to such an extent that it contains about 0.5 gram of

urea per litre, treated with concentrated Tanret's reagent (10 c.c.), and centrifuged. The clear liquid is treated under definite conditions with pure acetic acid and a 10% solution of xanthhydrol in absolute methyl alcohol; after three hours, the xanthylcarbamide is filtered through a Gooch crucible, washed with absolute methyl alcohol, dried at 70°, and weighed. H. W.

**Estimation of Urea by Xanthhydrol.** FRENKEL (*Ann. Chim. Anal.*, 1920, [ii], 2, 234—239).—Ten c.c. of a 10% solution of urine are treated with 35 c.c. of glacial acetic acid, and 1 c.c. portions of 10% xanthhydrol solution (in methyl alcohol) are added at intervals of ten minutes until 5 c.c. have been introduced. After one hour, the precipitate formed is collected, washed with alcohol, dried at 100°, and weighed; the weight is divided by 7 to obtain the amount of urea. Other substances found in urine do not give a precipitate with the reagent. The method may be applied to the estimation of urea in blood after this has been treated with mercuric chloride-potassium iodide reagent (mercuric chloride 2.71 grams, potassium iodide 7.20 grams, glacial acetic acid 66 c.c., and water 100 c.c.), and filtered. W. P. S.

**Micro-method for the Estimation of Urea in Blood and Organic Secretions.** K. L. GAD-ANDRESEN (*Biochem. Zeitsch.*, 1919, 99, 1—19).—The proteins are precipitated with 0.01*N*-acetic acid in the presence of sodium acetate, and the urea is estimated in the filtrate with sodium hypobromite. The nitrogen evolved is measured with Krogh's microrespirometer, and the result calculated by means of Krogh's formula. A correction is made for the nitrogen evolved by other substances. Only 0.1 c.c. or 0.15 c.c. of blood is required. The occasional error is of the magnitude of 0.5 mg. per 100 c.c. Comparisons with the urease method showed good agreement. This method is applicable to blood and various secretions of the organism. It is not suitable for the estimation of urea in muscle tissue. S. S. Z.

**Estimation of Hydrocyanic Acid.** R. LEITCH MORRIS (*Pharm. J.*, 1920, 105, 83—85).—Liebig's method (titration with silver nitrate solution) is trustworthy for the estimation of hydrocyanic acid provided that the acid is neutralised previously; any great excess of alkali must be avoided, and this is best attained by using borax solution in place of sodium hydroxide for the neutralisation (Guerin's modification). Excess of borax does not interfere. Volhard's method is useful in special cases, but entails the separation of the silver cyanide by filtration before the excess of silver nitrate can be titrated. Mohr's method (titration with silver nitrate after neutralisation with magnesium oxide, and using potassium chromate as indicator), and Denigès' modification of Liebig's method (titration in alkaline solution, using potassium iodide as indicator), are also trustworthy, but in the latter it is essential to use a sufficient quantity of potassium iodide. Fordos and Gelis' iodometric method is suitable for the estimation of cyanide in mercury cyanide. W. P. S.

**Hydrocyanic Acid in Phaseolus lunatus.** J. A. SIMPSON (*Anal. Acad. Cien. Med. Fis. Nat. Habana*, 1918—1919, **55**, 250—283; *Expt. Sta. Rec.* **42**, 7).—To estimate hydrogen cyanide, the crushed beans were heated with dilute sulphuric acid, and the distillate was collected in sodium or potassium hydroxide solution. This was heated with calcium polysulphide and titrated with 5% ferric sulphate until the colour of ferric thiocyanate developed. With care, the method is accurate to 0.00001 gram HCN. Of the varieties examined, "Rangoon blanca" gave 40 mg. HCN per 100 (grams?). Several gave between 3 and 8 mg. per 100 (grams?). The rest gave negative results. CHEMICAL ABSTRACTS.

**Modification of the Van Slyke Method for Estimating Arginine.** A. E. KOEHLER (*J. Biol. Chem.*, 1920, **42**, 267—268).—Van Slyke's method (compare A., 1916, ii, 62) is modified by drawing a slow current of air through the liquid during the digestion, the apparatus for absorbing the ammonia being a simple gas wash-bottle. W. G.

**Volumetric Estimation of Diazo-compounds by Reduction.** EDMUND KNECHT and LEONARD THOMPSON (*J. Soc. Dyers and Col.*, 1920, **36**, 215—219).—Benzenediazonium chloride in dilute hydrochloric acid solution may be titrated with titanous chloride solution, using H-acid as external indicator. The reaction requires two equivalents of hydrogen, and takes place without simultaneous formation of phenylazoimide and aniline. The titration may also be carried out by adding an excess of titanium trichloride solution and titrating the excess with acid-green solution in the presence of sodium tartrate. Methods are also described for the titration of sodium *p*-nitroisodiazobenzene with titanium trichloride solution or sodium hyposulphite solution. [See, further, *J. Soc. Chem. Ind.*, 1920, 594A.] W. P. S.

**Proteins and Some New Methods of Investigating their Composition.** A. C. ANDERSEN (*K. Vet. Landbohøjskole Aarskrift*, 1917, 308—334; from *Chem. Zentr.*, 1920, iv, 113).—Van Slyke's method of analysing proteins is modified by separating the fifth fraction (amino-nitrogen) into two sub-fractions; the first of these contains glycine, alanine, serine, phenylalanine, tyrosine, valine, and the three isomeric leucines as monoamino-monocarboxylic acids, whilst the second comprises the monoamino-dicarboxylic compounds, aspartic and glutamic acids. When an aqueous solution of a mixture of these amino-acids is neutralised with sodium hydroxide in the manner recommended by Sørensen for the formaldehyde titration, the monoamino-monocarboxylic acids, together with proline and oxyproline, remain uncombined, whilst the monoamino-dicarboxylic acids react with one equivalent of base. After evaporation of such a solution and incineration of the residue, sodium carbonate is left in amount equivalent to the monoamino-dicarboxylic acids present. Exact directions for performing the analyses are given. H. W.

**The Estimation of Hæmatin in the Whole Blood.** FRED VLÈS (*Bull. Soc. chim. Biol.*, 1920, 2, 125—132).—Two methods, depending on the transformation of a mixture of oxyhæmoglobin and hæmatin into one of reduced hæmoglobin and reduced alkaline hæmatin, or one of carboxyhæmoglobin and reduced alkaline hæmatin, respectively, are described. The estimation is carried out by spectrophotometric means. J. C. D.

**A Method for the Estimation of Methæmoglobin and Hæmoglobin in Blood.** W. S. McELROY (*J. Biol. Chem.*, 1920, 42, 297—300).—The total hæmoglobin (methæmoglobin + hæmoglobin) is determined colorimetrically as hæmoglobin, using potassium ferricyanide to convert the hæmoglobin into methæmoglobin. The oxygen capacity is determined by Van Slyke's method (compare A., 1918, ii, 82), from which is calculated the hæmoglobin. The difference between the two values is the amount of methæmoglobin. W. G.

**A Quantitative Method for Estimation of Vitamine.** ROGER J. WILLIAMS (*J. Biol. Chem.*, 1920, 42, 259—265. Compare A., 1919, i, 463).—It has been shown that the number of yeast cells produced from a single cell in eighteen hours under given conditions is a measure of the amount of vitamine present (compare Bachmann, A., 1919, i, 613). The method is now modified, and is gravimetric. A culture solution containing 20 grams of sucrose, 3.0 grams of ammonium sulphate, 2.0 grams of potassium phosphate, 1.5 grams of asparagine, 0.25 gram of calcium chloride, and 0.25 gram of magnesium sulphate in 1 litre of water is prepared. To 100 c.c. of this solution a known amount of the solution to be tested is added, and the mixture is made up to 110 c.c. and pasteurised or sterilised. To this is added 1 c.c. of freshly made yeast suspension containing 0.3 gram of fresh yeast per litre, and the whole is incubated for eighteen hours at 30°. A little formaldehyde is added to stop growth, any growth of wild yeast on the surface is removed by a copper gauze scoop, and the yeast is then filtered off on a Gooch crucible, washed with water, dried at 103° for two hours, and weighed. The weight of yeast thus obtained minus the weight obtained in a control is directly proportional to the amount of vitamine added. The results are expressed as a "vitamine number," this being the number of milligrams of yeast produced by 1 gram of the material tested. It has been shown by experiment that nothing except vitamine in the small amounts used will materially improve the medium, which already contains asparagine in addition to ammonium sulphate. W. G.

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## General and Physical Chemistry.

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### Refractivities of Saturated and Unsaturated Compounds.

GERVAIS LE BAS (*Trans. Faraday Soc.*, 1920, **15**, 231—237).—Further applications of the author's calculations to organic compounds (see A., 1918, ii, 49, 281). Negative anomalies are found with furfuraldehyde and thiophen. In pyridine there is an anomaly equal to that due to two and a-half ethenoid linkings. Other aromatic compounds, and substances containing the carbonyl group, are considered.

J. R. P.

### Size of the Alkali Cations and Halogen Anions.

ADOLPH HEYDWEILLER (*Zeitsch. Physik*, 1920, **1**, 393—394).—Refraction data are used as a check on values obtained by Born and Landé from Born's crystal-grating theory. For the methods, previous papers are referred to. The agreement is considered excellent, and favourable to Born's theory.

CHEMICAL ABSTRACTS.

### A Simple Spectrometer for Laboratory Use.

GÜNTER SCHEIBE (*Zeitsch. physiol. Chem.*, 1920, **110**, 229—232).—A description of a comparatively inexpensive form of spectrometer which has sufficient accuracy for ordinary purposes in a physiological laboratory.

S. S. Z.

### Spark Spectra of Various Elements in Helium in the Extreme Ultraviolet.

J. C. McLENNAN and A. C. LEWIS (*Proc. Roy. Soc.*, 1920, [A], **98**, 109—114).—The new wave-lengths 1745 Å.U., 1742.5 Å.U., and 1657 Å.U., have been observed in the spectrum of silicon. The spectra of tellurium, molybdenum, and zirconium were examined, and the results tabulated. These are considered to be correct to 0.5 Å.U. A strong doublet appears common to all the spectra in the neighbourhood of 1745 Å.U., probably due, according to Lyman, to silicon. A strong line at 1656.7 Å.U. was found on all the plates, which Lyman gives as present in all metallic spark spectra in helium. It was probably due to carbon from the decomposition of carbon monoxide given off from the wax joint. In the spectra of molybdenum and zirconium all the wave-lengths observed were of weak intensity. The radiations from tellurium were stronger, and their relative intensities are given in the table. A reproduction of the spectrum of this element is given.

J. R. P.

### Arc Spectra in Vacuum and Spark Spectra in Helium of Various Elements.

J. C. McLENNAN, J. F. T. YOUNG, and H. J. C. IRETON (*Proc. Roy. Soc.*, 1920, [A], **98**, 95—108. Compare A., ii, 458, 459).—The vacuum arc spectra of antimony, bismuth, calcium, magnesium, selenium, silver, and copper, and the spark

spectra in helium of antimony, bismuth, cadmium, lead, magnesium, thallium, and tin, have been investigated in the region below 1850 Å.U. The work with the vacuum grating spectrograph has resulted in the extension of the vacuum arc spectrum of copper to about 1216 Å.U.

J. R. P.

### Air Lines in Spark Spectra from $\lambda$ 5927 to $\lambda$ 8719.

PAUL W. MERRILL (*Astrophys. J.*, 1920, **51**, 236—243).—In observing the spectrum of any element, if the source is the spark in air, there are a large number of lines due to the air itself, which it is impossible to eliminate. In order to be able to distinguish the lines due to the various components of the atmosphere, the author has observed the spark in air and in oxygen, using several different elements as electrodes. The wave-lengths of 58 air lines are given in a table. Because of the ill-defined nature of these lines, the accuracy is not very great. Twenty of the list correspond with known lines of hydrogen, nitrogen, oxygen, or argon, including six lines of the red spectrum of argon and four of oxygen lines which had not previously been observed in spark spectra. Two others are probably due to oxygen; the rest have not as yet been identified. All the identified lines are found to be shifted toward the red with respect to vacuum tube wave-lengths. This increase in wave-length amounts to about 0.1 Å. for the oxygen lines, 0.6 Å. for the argon lines, 0.7 Å. for the hydrogen  $\alpha$ -line, and varies from 0.1 Å. to 0.7 Å. for the nitrogen lines. On introducing self-induction the only marked change is the weakening of the nitrogen lines  $\lambda\lambda$  6482 and 6610. Using as source the condensed spark in an atmosphere of commercial oxygen, several identifications of oxygen and nitrogen lines previously observed in the vacuum tube were confirmed, and the doubtful identification of  $\lambda$  7157 as due to oxygen is strengthened.

CHEMICAL ABSTRACTS.

**Vacuum Grating Spectroscopy.** J. C. McLENNAN (*Proc. Roy. Soc.*; 1920, [A], **98**, 114—123).—It would appear that in the spectroscopy of the ultraviolet the procedure to be followed which would permit of the most rapid progress being made would be, so far as emission spectra are concerned, to work with a vacuum grating spectrograph and to use an atmosphere of helium. There is evidence to show that this gas is transparent to wave-lengths as short as 400 to 500 Å.U., or even shorter. As regards absorption spectra, it is shown that if a vacuum grating spectrograph, provided with a lamp of the "Pointolite" type, is filled with helium to a suitable pressure, arcs can be struck in the gas, when the requisite voltages are applied, which will provide a radiation consisting of wave-lengths extending probably near to 400 Å.U. By interposing vapours of elements between the arc and the grating of the spectrograph, it should be possible to obtain the absorption spectra of the elements vaporised. An improved apparatus is described, and preliminary measurements made down to 1025.8 Å.U., although indications were obtained on all the plates of a

faint continuous spectrum extending to well below 500 Å.U. The potential fall between the electrodes was only 45 volts. J. R. P.

**Existence of a Relation between the Heads of Banded Spectra.** TOKIHARU OKAYA (*Proc. Phys. Math. Soc. Japan*, 1919. [3], 1, 332—343. Compare this vol., ii, 140).—The relations  $\lambda/\lambda' = \sqrt{m/m'}(p/q)^{3/2}$  and  $p/q = a/a'$  between the heads of bands due to different elements of the same group in the periodic system, where  $\lambda$  and  $\lambda'$  are the wave-lengths of the heads of the bands,  $m$  and  $m'$  the atomic weights,  $p$  and  $q$  integers smaller than ten, and  $a$  and  $a'$  the radii of the atomic models of Nagaoka, are open to the criticism that there are so many heads in the spectra of the gold group and the alkaline earth group examined previously that the above relations may have been due to chance. In the present paper, by choosing elements the spectra of which have few heads, such as palladium and nickel, it is shown that the above relations hold only for elements in the same group, and do not hold for elements of different groups. Other elements for which the relations hold are vanadium, columbium, and tantalum. The conclusion is drawn that the oxide of vanadium at the moment of emission of band spectra assumes the form  $\text{VO}_2$  and not  $\text{V}_2\text{O}_5$ , which is the form stable at ordinary temperatures.

CHEMICAL ABSTRACTS.

**Fluorescence of the Uranyl Salts.** EDWARD L. NICHOLS, HORACE L. HOWES, ERNEST MERRITT, D. T. WILBER, and FRANCES G. WICK (*Carnegie Inst. Washington Publication*, 1919, 298, 1—241).—The historical introduction is followed by chapters devoted to: structure of fluorescence spectra; preliminary observations on certain uranyl salts; phosphorescence of the uranyl salts; intimate structure on cooling to  $-185^\circ$ ; polarised spectra of double chlorides; the nitrates and phosphates, water of crystallisation, crystalline form; the acetates; the sulphates; and frozen solutions. Since the fluorescence of certain uranyl compounds is resolved into groups of narrow line-like bands when these compounds are excited to luminescence at very low temperatures, a study of the fluorescence has been undertaken. The spectra of numerous uranyl salts have been mapped. Owing to the extraordinarily complex character of the phenomena, no satisfactory theory has as yet been evolved, but the mass of facts recorded and the general principles established will, it is hoped, afford a basis for the successful theoretical development of this important and little understood branch of the science of radiation. Appendices are devoted to the chemistry and crystallography of the uranyl salts, and to the subject of phosphoroscopes.

CHEMICAL ABSTRACTS.

**Optical Rotation, Optical Isomerism, and the Ring Electron.** H. STANLEY ALLEN (*Phil. Mag.*, 1920. [vi], 40, 426—439).—A theoretical paper in which an hypothesis of optical rotation is advanced in which the electron, instead of being

regarded as a point charge, is looked on as an anchor ring of negative electricity rotating rapidly about its axis as suggested by Parson (Smithsonian Misc. Coll., No. 2371, Nov., 1915). Such a ring electron vibrating in a linear path takes the place of an ordinary electron moving in a spiral path as postulated by Drude. It is shown that a rotation of the plane of polarisation of light will result, and an expression is found for the amount of rotation per unit length. Employing the theory of atomic structure due to Lewis and Langmuir (A., 1916, ii, 310; 1919, ii, 328), a graphical representation may be obtained for the dextro- and lævo-rotatory forms of a compound. The experimental facts with regard to optical activity are in good agreement with the hypothesis put forward, which may be applied not merely to carbon compounds, but to any compound containing an asymmetric atom. On the assumptions made it is possible to deduce that eight isomerides of cinnamic acid may exist.

J. F. S.

**Influence of Constitution on the Rotation of Optically-active Substances. XI. Normal and Abnormal Rotation Dispersion and its Calculation.** H. RUPE and ARTHUR AKERMANN (*Annalen*, 1920, **420**, 1—32. Compare A., 1917, i, 539, and previous abstracts).—An examination of more than fifty dispersion curves leads the authors to the conclusion that the normal rotatory dispersion of organic substances can be expressed by the simple formula  $\alpha_n = K/\lambda_n^2 - \lambda_0^2$ , in which  $K$  is the "rotation constant" and  $\lambda_0^2$  is the dispersion constant; the expression has been used previously by Lowry and Dickson (T., 1915, **107**, 1173). The formula is shown to be applicable to liquids in substance and in solution; it gives results which are in good harmony with the observed data over the visible spectrum, and can probably be also employed outside these limits.

In previous communications, Rupe has endeavoured to distinguish between normal and abnormal rotatory dispersion on the basis of the displacement of the "characteristic wave-length"; it now appears that when a substance exhibits abnormal dispersion within the region of measurement, the characteristic wave-length differs from the mean of the respective class of compounds, but, although strong displacement is necessary for abnormal dispersion, it is not by itself sufficient.

The methods of calculating the values of  $K_0$  and  $\lambda_0^2$  are fully discussed, and it is shown that, provided the dispersion is normal, the calculated values for the specific rotations of a large number of compounds for a given wave-length agree with the values observed within the limits of experimental error. The following criteria of abnormal dispersion are then deduced, in which three types are distinguished: (i) Apparently normal rotatory dispersion with greatly displaced dispersion curve; the divergence between the calculated and observed values does not amount to more than three times the mean experimental error, but  $\lambda_0^2$  and  $\lambda_c$  differ markedly from the mean value for the appropriate class of compound.

(ii) Relative abnormal rotatory dispersion, in which the differences are from three to five times as great as the mean experimental error; and (iii) Total abnormal rotatory dispersion, in which the differences exceed fifteen times the mean experimental error.

The connexion between optical activity and constitution is discussed at length, and it is pointed out that comparisons between molecular rotations observed with a single wave-length are inadequate for the elucidation of the problem, and that the rotatory dispersion must also be ascertained. The latter is greatly influenced by the solvent used, and, at present, this action does not appear to be exerted in any regular manner even towards substances of the same type. The influence of constitution on  $K_m$  is described, and it is found that if the added radicle is an aliphatic saturated hydrocarbon group and if the chemical change does not involve any considerable change in the optical properties of the asymmetric complex,  $K_m$  remains approximately constant in homologous series. The rule also applies when aromatic groups are introduced, provided that at least one methylene group lies between the aromatic radicle and the asymmetric complex.  $K_m$  is increased by the introduction of one or more ethylenic linkings, by a triple bond (the effect of this is noticeably less than that of two double bonds), and by the direct attachment of an aromatic nucleus to the asymmetric complex. Changes in  $K_m$  are also induced by one or more groups containing oxygen. It thus appears that  $K_m$  is not affected by the number of groups required to form the molecule, but is mainly dependent on the spatial distribution of the atoms and the relative distances from one another.

H. W.

### Activation of Photochemical Elements with Silver Haloid Electrodes and their Application.

SATOYASU IIMORI and TOSHIMASA TAKEBE (*J. Tokyo Chem. Soc.*, 1920, **41**, 77—185).—The mechanism and sensitisation of the Becquerel effect and the application of the photochemical cell for measuring candle-power are extensively considered. In order to obtain the most stable maximal photovoltaic effect the silver haloid electrodes are prepared as follows: A small silver plate is soaked in haloids of iron, copper, mercury, or thallium; later its surface is freed from the solutions by use of suitable solvents, and it is placed in a solution of iodine in alcohol, benzene, chloroform, or ether. The final coating of the electrodes with iodide is perfected by placing them in 0.3—5 *M*-potassium iodide saturated with silver iodide. Such an electrode, after several days, becomes exceedingly sensitive, and contains a permanent film. Proper concentration of potassium iodide is very important. The cells of 20 c.c. and 90 c.c. capacity are made of glass, with ebonite covers. The outer surface is covered with tin foil except the window, which admits the light and behind which one of the electrodes is placed. A solution of potassium iodide is also used for the cell. The *E.M.F.* is measured by Poggendorff's method, the Weston cell being used as standard. Several factors for obtaining maximal photovoltaic effect are studied. The effect of

concentration of the cell liquid is expressed by  $\pi_m = A + B \log 1/C$ , in which  $\pi_m$  is in millivolts,  $C$  = concentration of potassium iodide,  $A$  and  $B$  are constants due to temperature, degrees of illumination, electrodes, etc. Rise of temperature lowers the effect, its extent depending on the illumination and characters of the cell. The effect of intensity of illumination is expressed by  $\pi_m = \sigma(1 - e^{-KE\alpha})$ , where  $E$  is the intensity;  $\sigma$ ,  $K$ , and  $\alpha$  are constants for cells, temperature, and wave-length. For a limited condition, a much simpler formula,  $\pi_m = a \log E - b$ , can be used. The effect of the size of windows is given by  $\pi_m = \rho(1 - e^{-hA\beta})$ , where  $A$  = area of window, which is always smaller than that of the electrode, and  $\rho$ ,  $h$ , and  $\beta$  are constants. The time required to attain the maximal effect is greater with rise of temperature and concentration of potassium iodide, and smaller with increase of illumination and size of the window. The time required to decrease to the half of the maximal value after the light is removed is greater with the larger concentration of the liquid, but is independent of the intensity of illumination and the size of the window. Theoretical explanations for all factors are given. Considering the effect of temperature and nature and concentrations of the liquid used for the battery, it is concluded that the photovoltaic effect produced with haloid electrodes must be caused by reversible chemical reaction of the silver iodide, which takes place in the following order: at the exposed electrode  $mn \text{ AgI} \rightarrow mn \text{ Ag} + mn \text{ I}$ ,  $mn \text{ I} \rightarrow m \text{ I}' n + m \oplus$  becoming  $\oplus$ ; at the unexposed electrode,  $mn \text{ AgI} \rightarrow mn \text{ Ag} + m \text{ I}' n + m \oplus$ ,  $mn \text{ AgI} + m \text{ I}' n \rightarrow mn \text{ AgI} + m \ominus$ ,  $mn \text{ AgI} \rightarrow mn \text{ AgI} + m \oplus$ ,  $\oplus \ominus = 96540$  coulombs.

CHEMICAL ABSTRACTS.

**The Mechanism of Chemical Actions Provoked by X-rays.** A. DAUVILLIER (*Compt. rend.*, 1920, 171, 627—629).—The mechanism suggested is that the cause of the chemical action is the destruction of the negative ions, which alone can lose their electrons by the impact of the rapid electrons constituting the corpuscular radiation. The corpuscles, slowly expelled, neutralise the adjacent positive ions, the electronegative and electropositive elements thus being liberated in the atomic state. These produce colorations in solid or viscous substances and chemical changes in media where they are mobile. Several reactions are examined in the light of this hypothesis.

W. G.

**Explanation of Röntgen Spectra and the Constitution of Atoms.** ADOLF SMEKAL (*Physikal. Zeitsch.*, 1920, 21, 505—506).—The theories of Vegard (A., 1919, ii, 129) and of Kroo (A., 1918, ii, 303) are discussed. The calculations of Vegard do not do justice to the most exact measurements of Siegbahn (A., 1919, ii, 261), whereas the formula of Kroo appears to apply with great accuracy. The conclusions of Vegard as to the structure of atoms are thereby vitiated.

J. R. P.

**The X-ray Absorption Spectra of Phosphorus.** J. BERGENGREN (*Compt. rend.*, 1920, 171, 624—626).—In the

X-ray absorption spectra of the different varieties of phosphorus, the author finds that the wave-lengths of the limits of absorption are different for black phosphorus and for phosphorus in the form of phosphoric acid. That of red phosphorus shows a double limit, one component of which is identical with that of black phosphorus, and the other, attributed to yellow phosphorus, coincides, at least approximately, with that of phosphoric acid. W. G.

**The Fine Structure of the Discontinuities of Absorption in X-ray Spectra.** M. DE BROGLIE and A. DAUVILLIER (*Compt. rend.*, 1920, 171, 626—627).—A discussion of Kossel's work (compare *Zeitsch. Physik*, 1920, 1, 119) in the light of Bergengren's work on phosphorus (compare preceding abstract).

W. G.

**Precision Measurements in the K-series of X-rays. Elements from Copper to Sodium.** ELIS HJALMAR (*Zeitsch. Physik*, 1920, 1, 439—458).—Siegbahn's vacuum spectrograph has been used in making wave-length measurements. Several new weak lines are found, besides the component of  $\beta$  predicted by Sommerfeld. These are: one in the neighbourhood of  $\beta$ , a close doublet of shorter wave-length than  $\alpha_3\alpha_4$ , and a line between  $\alpha_1$  and  $\alpha_3$ . Not all these occur in any one element. The relation  $n_\lambda = 2d \sin \phi$  is tested by comparing the angle of reflection of the same line in different orders. The lattice constant for gypsum is measured as  $\log 2d = 1.1805620 - 8(\pm 0.0000149)$ .

CHEMICAL ABSTRACTS.

**Origin of the Iodine Band Spectrum and its Place in the Quantum Theory.** W. STREUBING (*Zeitsch. Physik*, 1920, 1, 426—430).—The iodine band spectrum results from neutralisation of the ionised atoms and their combination to form the molecule. The high frequency limit of the spectrum gives, on the quantum theory, the work necessary for the decomposition from molecules to ions. This has been calculated by Born (*A.*, 1919, ii, 214) on the space-lattice theory, and the agreement is quantitative.

CHEMICAL ABSTRACTS.

**Fine Structure of the Near Infra-red Absorption Bands of the Halogen Acids.** WALTER F. COLBY (*Astrophys. J.*, 1920, 51, 230—235).—A quantum theory of the fine structure in the infra-red absorption spectra of the diatomic gases is put forward. The postulate of Bjerrum (*Nernst Festschrift*, 1912, 90), that the fine structure of these bands is due to the rotation of the molecules in stationary states corresponding with the quantum relation, has proved very fruitful. The present paper proposes to test the hypothesis by comparing the theoretical results, for the simplest molecule model of the Bohr type with the experimental results recently obtained by Imes (*Astrophys. J.*, 1919, 50, 251) for the halogen acids. For hydrogen fluoride, chloride, and bromide, the observed interatomic vibration frequencies are

respectively 38, 40, and 47% less than the theoretical, whilst the computed separations of the pairs of nuclei are, respectively, 38, 54, and 59% less than the values given by Ives. The variation with mass is explained as a screening effect which has been neglected in the elementary theory. The agreement between theory and experiment is sufficient to lend support to the Bjerrum hypothesis, and suggests the importance of developing a more adequate theory involving fewer simplifying assumptions.

CHEMICAL ABSTRACTS.

**Structure of the Helium Atom.** IRVING LANGMUIR (*Science*, 1920, **51**, 605—607).—The ionisation potential as calculated from Bohr's theory, 28·8 volts, does not agree with the experimental value, 25·4 volts. By means of Landé's theory of the transference of momentum from one electron to another around the nucleus rather than a rotation of the electrons themselves, the author has calculated the numerical dimensions of the path of the electrons in the helium atom after four approximations to within 0·1%. Each electron travels through less than half an orbit when it is reflected back on approaching the other electron.

CHEMICAL ABSTRACTS.

**Helium and Parhelium.** J. FRANCK and F. REICHE (*Zeitsch. Physik*, 1920, **1**, 154—160).—There are two separate systems of spectral series for helium which belong to helium and to parhelium. In helium the electron orbits are coplanar, whilst in parhelium they are at an angle to each other, as described by Landé. Parhelium is the less stable, and its ionisation potential is the one determined experimentally. The base line for the principal series for helium is 10,830 Å. and for parhelium is 20,582 Å., and is caused by the return, in each case, to a diquantal orbit. For normal helium, that is, unquantal, the resonance potential, in agreement with the calculations of Landé, would lead to a ground line of about 600 Å. A change from a higher quantum orbit of one system to a lower of the other never occurs. Parhelium is the normal condition of the element (unquantal).

CHEMICAL ABSTRACTS.

**Aggregate Recoil during the Decomposition of  $\alpha$ -Radiating Substances.** ROBERT W. LAWSON (*Wien Anz.*, 1919, 86—88; from *Chem. Zentr.*, 1920, iii, 431).—It has been observed repeatedly that polonium which has been deposited electrolytically on metallic foil activates objects in its immediate vicinity. The following explanation of the phenomenon is advanced. The polonium lies on the metallic support in aggregates of atoms. When an  $\alpha$ -particle is discharged from such an aggregate, the latter receives the recoil in the opposite direction and leaves the support. The author designates the phenomenon "aggregate recoil," and examines its dependence on the nature of the supporting metal and on the prevalent gas pressure. The importance of the recoil on the estimation of the life period of polonium is discussed.

H. W.



**Rapid Graphic Method of Estimating Radium.**

N. E. DORSEY (*Physical Rev.*, 1919, **14**, 173; from *Chem. Zentr.*, 1920, iii, 399).—The increase in the  $\gamma$ -radiation of a radium preparation from the time  $t_1$  to  $t_2$  is denoted by the expression  $J_2 - J_1 = 1.0089 \cdot e^{-\lambda t_1} (1 - e^{-\lambda(t_2 - t_1)}) \cdot J_\infty$ , where  $\lambda$  is the rate of decay of the emanation and  $J_\infty$  the equilibrium value. If the observed values of  $J$  are plotted against  $(1 - e^{-\lambda t})$ , in which  $t$  is calculated from any desired instant, a straight line is obtained, the intersection of which with the ordinate for  $t = \infty$  gives the equilibrium value  $J_\infty$ , which can thus be graphically determined. H. W.

**Radium Content of the Rocks of the Loetschberg Tunnel.** J. H. J. POOLE (*Phil. Mag.*, 1920, [vi], **40**, 466—471).—

The radium constant of 82 specimens of rocks collected at different points in the Loetschberg Tunnel has been estimated by the fusion method. The content is found to be fairly constant throughout the whole length, a mean value  $2.2 \times 10^{-12}$  grams per gram of rock being obtained. This value is obtained from values lying between  $0.8 \times 10^{-12}$  from a talc schist obtained 480 m. from the south end of the tunnel, and  $6.5 \times 10^{-12}$  from a felspar talc schist obtained 395 m. from the south end. For individual rocks, the following mean values were obtained: granite (7 specimens),  $2.3 \times 10^{-12}$ ; limestone (16 specimens),  $1.5 \times 10^{-12}$ ; talc schist (16 specimens),  $2.0 \times 10^{-12}$ ; quartz schist (12 specimens),  $2.4 \times 10^{-12}$ ; mica schist (2 specimens),  $2.1 \times 10^{-12}$ ; hornblende schist (2 specimens),  $3.1 \times 10^{-12}$ ; schist lustré (2 specimens),  $3.4 \times 10^{-12}$ ; felspathic schist (3 specimens),  $2.7 \times 10^{-12}$ ; unclassified schists (16 specimens),  $2.5 \times 10^{-12}$ ; aplite (2 specimens),  $2.5 \times 10^{-12}$ ; quartz porphyry (1 specimen),  $2.5 \times 10^{-12}$ ; anhydrite (2 specimens),  $1.1 \times 10^{-12}$ ; and quartz sandstone (1 specimen),  $4.3 \times 10^{-12}$ . The mean radium constant of 53 schists is  $2.4 \times 10^{-12}$  grams per gram of rock. J. F. S.

**Atmospheric Electricity. LXI. Measurement of the Radium Emanation Content of the Air at Innsbruck.** RELY

ZLATAROVIC (*Wien Anz.*, 1920, 75; from *Chem. Zentr.*, 1920, iii, 334).—By the use of charcoal and petroleum as absorbents, an ionisation vessel which previously showed a saturation current,  $i_1$ , was completely freed from emanation; the saturation current,  $i_2$ , which was now measured, was found to be constant. The difference,  $i_1 - i_2$ , is applied to the calculation of the emanation content, and, as a mean of forty-nine observations, gives the value  $433 \times 10^{-18}$  Curie/c.c., the extreme values being 1110 and 40. Dependence on meteorological factors could only be so far recognised in that rainy periods correspond with lower emanation values. H. W.

**Effects of Electron Collisions with Atmospheric Neon.**

FRANK HORTON and ANN CATHERINE DAVIES (*Proc. Roy. Soc.*, 1920, [A], **98**, 124—146).—The minimum radiation velocity was found to be 11.8 volts with neon at an average pressure of 0.133 mm.

The minimum ionisation velocity was found to be 16·7 volts. The second radiation velocity was found to be 17·8 volts. The second and third ionisation velocities were found to be 20·0 and 22·8 volts respectively. The existence of three critical ionisation velocities and two critical radiation velocities indicates that neon differs more in constitution from helium and argon than would be expected from its position in the table of the elements. The accepted view of the connexion between the quantities of energy required for the production of radiation and of ionisation is that they correspond with the first and with the limiting frequency, respectively, of some particular spectral series of the element concerned. On this view, it would be expected that with every ionisation velocity there would be associated a definite radiation velocity. In the experiments, evidence of three ionisation velocities, but of only two radiation velocities, was obtained. The two radiation velocities may occur so close together that they do not give separate indications on the curves, in which case one might escape detection. Another possibility is that the ionisation observed at one of the three critical velocities is a spurious effect. The minimum radiation velocity of helium is 20·4 volts, close to the value 20·0 volts found above. The radiation velocity of 11·8 volts appears to be associated with the ionisation velocity of 16·7 volts, and the radiation velocity of 17·8 volts with the ionisation velocity of 22·8 volts. If neon consists of two or more constituents having different radiation and ionisation velocities, the critical velocities 11·8 and 16·7 are to be attributed to one, and the values 17·8 and 22·8 to the other.

J. R. P.

**Constancy of the Ratio of Actinium to Uranium in Natural Minerals.** STEFAN MEYER and VIKTOR F. HESS (*Sitzungsber. K. Akad. Wiss. Wien*, 1919, **128**, [2a], 909—924; from *Chem. Zentr.*, 1920, iii, 435—436).—It has been assumed for a long time that the actinium series is derived by indirect degradation of the uranium-radium series. If this is the case, the ratio of actinium to uranium or radium must be constant in all uranium minerals. Few, and not very concordant, observations have been recorded, chiefly by Boltwood, in this connexion. The authors have therefore examined exhaustively the reputed constancy of the ratio  $\text{Ac}:\text{U}$ , and have used uranium minerals which differ as widely as possible from one another, both in origin and composition, and include the following: amorphous Joachimsthal pitchblende, crystalline pitchblende from Morogoro, bröggerite, and two different specimens of thorianite. Quantities of the minerals corresponding with 30 grams of uranium were dissolved in concentrated nitric acid, and the solutions were diluted with water to 1 litre and brought into rotating flasks; the radium emanation was first removed in a constant current of air, and, immediately afterwards, the active precipitate of actinium (with a portion of thorium precipitate if present) was collected on a negatively charged plate. The value of  $\text{Ac} \cdot B + C$  could be readily derived from the known half life-periods for  $\text{Ac} \cdot B + C$  and

Th-*B* + *C*. The observed activities are not great, but the results of repeated measurements are quite concordant. The ratio Ac:U is found to be constant in all minerals, thus giving a sure support for the hypothesis that the actinium series is genetically related to uranium. H. W.

**Ionisation in the Solar Chromosphere.** MEGH NAD SAHA (*Phil. Mag.*, 1920, [vi], **40**, 472—488).—From a discussion of the high-level chromospheric spectrum, it is shown that this region is mainly composed of ions of calcium, barium, strontium, scandium, titanium, and iron, whilst in the lower layers both ions and atoms occur. An attempt is made to account for these facts from the point of view of Nernst's theorem of the reaction isobar, by assuming that the ionisation is a type of reversible chemical process taking place according to the equation  $\text{Ca} \rightleftharpoons \text{Ca}^+ + e - U$ . The energy of ionisation, *U*, can be calculated from the ionisation potential of the elements. For the determination of the chemical constant and the specific heat, the electron is assumed to be a monatomic gas with an atomic weight 1/1836. The equation shows the great influence of pressure on the relative degree of ionisation. The almost complete ionisation of calcium, barium, and strontium in the high-level chromosphere is due to the low pressure in these regions. The calculated values are in good agreement with the experimental values of King (*Astrophys. J.*, **48**, 13). Hydrogen is completely dissociated into atoms at all points in the solar atmosphere. It is also shown that the greater the ionisation potential of an element, the less readily does ionisation occur under a thermal stimulus. Calculations have been made in the case of hydrogen (*V* = 13.6 volts) and helium (20.5 volts) which show that these elements are not ionised to an appreciable extent anywhere in the sun. Helium is ionised only in stars of the highest temperature (>16000° *K*), which therefore alone can show the Rydberg line 4686 and the Pickering lines  $\nu = N[1/2^2 - 1/(1 + 1/2)^2]$ .

J. F. S.

**Relative Ionisation Potentials of Gases as Observed in Thermionic Valves.** G. STEAD and B. S. GOSSLING (*Phil. Mag.*, 1920, [vi], **40**, 413—425).—A method is described whereby the ionisation potential of gases may be determined. This method consists in determining the differences of potential which are necessary for the production of positive ions in soft thermionic valves. The tube used was a three-electrode valve of the usual form, the cold electrodes being connected together. Next to the tungsten filament there was a molybdenum spiral, 0.4 mm. diam., coiled into a helix of 4.5 mm. diam., and having four to five turns per cm. Outside this was a nickel cylinder 10 mm. diam. When an appreciable quantity of a gas is present in such a tube, the voltage-current curve changes, at a definite potential, from the high vacuum characteristic. This point represents the beginning of the emission of positive ions and gives the ionisation potential of the gas. Experiments have been carried out with mercury

vapour, argon, hydrogen, carbon monoxide, nitrogen, and helium at several pressures, and the following values found for the ionisation potential: mercury, 10·8 volts; argon, 12·5 volts; hydrogen, 15·0 volts; carbon monoxide, 15·0 volts; nitrogen, 17·2 volts; and helium, 20·8 volts. The value obtained for carbon monoxide differs from that obtained by other observers, and it is suggested that this does not represent a true ionisation potential, but rather a photo-electric effect. The present method of work is not open to the criticism offered to most methods of determining ionisation potentials.

J. F. S.

**Effect of a Trace of Impurity on the Measurement of the Ionisation Velocity for Electrons in Helium.** FRANK HORTON and DORIS BAILEY (*Phil. Mag.*, 1920, [vi], **40**, 440—450).—The ionisation potential of helium has been redetermined with perfectly pure gas and the effect of impurities on this value investigated. The results emphasise the importance of maintaining the helium perfectly pure when investigating the ionisation of gas by electron collisions. The only satisfactory method when a glass apparatus is used is to have a slow circulation of freshly purified helium through the ionisation chamber during the experiments. It is possible that if fused silica were substituted for glass, contamination of the gas would be less likely to occur. The ionisation curves indicate that the minimum ionisation velocity for electrons in helium is 25·0 volts, a value rather lower than that obtained by Horton and Davis (*A.*, 1919, ii, 210). The present results also indicate that the minimum radiation velocity for electrons in helium is 21 volts; but this value is no doubt too high, for the point at which ionisation of the impurities by the helium radiation was detected depended on the amount of impurity present, and was probably always higher than the point at which radiation was first produced from the helium atoms.

J. F. S.

**Ionisation Potential of Hydrochloric Acid and the Electron Affinity of Chlorine.** PAUL D. FOOTE and F. L. MOHLER (*J. Amer. Chem. Soc.*, 1920, **42**, 1832—1839).—The experiments indicate that the collision of an electron of sufficient velocity with a molecule of hydrogen chloride results in the immediate production of a positively charged atom of hydrogen and a negatively charged atom of chlorine. The ionisation causes disruption of the bond between the two ions in the molecule. The work necessary to ionise a gram-molecule of hydrogen chloride is accordingly the work of ionising a gram-atom of hydrogen plus the heat of formation of hydrogen chloride plus the heat of dissociation of 0·5 gram-molecule of chlorine minus the electron affinity of a gram-atom of chlorine. This, expressed in volts and referred to a single molecule, is 13·7 volts, in excellent agreement with the experimentally determined value, 14·0 volts. The electron affinity of chlorine is calculated as 4·8 volts. Hydrogen chloride is not known to possess any characteristic visible or ultraviolet

spectrum, in agreement with the observed peculiar type of ionisation and the absence of a resonance potential. Any radiation emitted which is characteristic of hydrogen chloride would be produced by the union of the hydrogen ion and the chlorine ion, giving rise to a quantum of  $h\nu = eV$ , where  $V = 14.0$  volts. The corresponding wave-length in the extreme ultraviolet is  $\lambda = 880 \text{ \AA.U.}$ , which could be observed, though with difficulty. A high voltage discharge through hydrogen chloride shows the ordinary spectrum of hydrogen. The attraction between a hydrogen nucleus and a halogen atom is about the same as the interaction between a hydrogen nucleus and the electron in the neutral hydrogen atom, as predicted by Haber.

J. R. P.

**Ionisation Potentials of Argon, Nitrogen, Carbon Monoxide, Helium, Hydrogen, and Mercury and Iodine Vapours.** CLIFTON G. FOUND (*Physical Rev.*, 1920, 15, 132—133).

—The object was to determine the effect of gas on the volt-ampere characteristics of a two-electrode electron discharge tube, and to determine the voltage at which the gas affected the space charge of the tube or ionisation potential. By the use of a commutator, the heating circuit along the filament was broken while the space current was measured, so that the current,  $i = A(V - V_0)^{3/2}$ , where  $V_0$  is the voltage equivalent to the initial velocity of the ions. The ionisation potential for argon was 15—16 volts at 1—200 bars pressure. With increase in filament temperature, due to the increased  $V_0$ , the potential was lowered. Nitrogen gave about 16 volts, carbon monoxide 13.5—14, mercury vapour 10—11, iodine vapour 8.5, whilst the values 20.5 for helium and 15 for hydrogen were uncertain.

CHEMICAL ABSTRACTS.

**Ionisation Potential of Mercury Vapour as a Function of the Temperature of the Cathode.** T. C. HEBB (*Physical Rev.*, 1920, 15, 130).

—Values as low as 3.2 volts were obtained for the ionisation potential of mercury vapour at very high temperatures. The striking voltage,  $V = 10.5 - 0.002T$ , where  $T$  is the absolute temperature.

CHEMICAL ABSTRACTS.

**Ignition of Gases at Reduced Pressures by Transient Arcs.** W. M. THORNTON (*Phil. Mag.*, 1920, [vi], 40, 450—460).

—The ignition of hydrogen, methane, ethane, pentane, propane, carbon monoxide, and coal gas by both direct- and alternating-current arcs has been investigated at a number of reduced pressures. The ignition current is plotted against the pressure, and curves produced in all cases. With direct-current arcs, the ignition current falls rapidly to a minimum with increase in pressure, and then rises equally rapidly to a maximum, after which it falls slowly to a constant value. The lower limit is found in all cases at about 0.2 atm., whilst the rapid rise lies between 0.4 and 0.5 atm. A mean ordinate (current in amperes) lies at the points:

hydrogen 0.30 ampere, methane 1.20 amperes, ethane 1.12 amperes, propane 0.87 ampere, and pentane 0.66 ampere, and these mean values may be expressed by the equation  $i = 0.334 + 23.5/\text{mol. wt.}$  The relative influence of hydrogen and carbon on the inflammability of the hydrocarbons is given by the equation

$$(i - i_0) = \alpha n_C / (n_H)^2,$$

where  $i$  is the ignition current of the hydrocarbon,  $i_0$  that of hydrogen,  $\alpha$  a constant,  $n_C$  and  $n_H$ , respectively, the number of carbon and hydrogen atoms. Two causes effect ignition, a thermal cause and an ionisation cause; either of these causes may be predominant, depending on conditions, and the form of the ignition curve depends on which of these causes is operative. With alternating current, the form of the curves is very much changed; in the case of hydrogen, the curve falls rapidly to 0.23 ampere, and then rises to 0.26 ampere, after which it falls to a steady value of about 0.1 ampere. With methane, there is only the slightest tendency for the curve to rise after the preliminary fall, but there is a halt, and then a slower fall to a stationary value. In the case of ethane and propane, the curve is of the same shape as that of methane, but the flat halt is very much longer. Coal gas is about ten times as inflammable as carbon monoxide. The whole of the curves given are reminiscent of the critical gas isothermal.

J. F. S.

**Electrolysis of Solutions of Sodium Nitrite using a Silver Anode.** F. H. JEFFERY (*Trans. Faraday Soc.*, 1920, **15**, 16—20).—

The reactions at the anode during the electrolysis of solutions of sodium nitrite of different concentrations in a divided cell, with a silver anode and platinum cathode, were investigated. In no case was silver deposited on the cathode. Silver dissolved from the anode, no gas being evolved. A deposit formed on the anode, which was found to be silver nitrite, together with a small percentage of finely divided silver from the disintegration of the anode. Measurements of the anode potential were made, and the results showed that in the immediate neighbourhood of the anode the concentration of silver ions was not increased by the nitrate ions. A complex salt,  $\text{NaAg}(\text{NO}_2)_3$ , was isolated at the anode in small, well-shaped, bright yellow crystals by electrolysis of an anolyte of 50 grams of sodium nitrite in 100 grams of water for fifty-five hours with a current of 0.072 ampere. The solution was allowed to evaporate isothermally over concentrated sulphuric acid in an exhausted desiccator. Further evaporation led to the separation of a mixture of this salt and sodium nitrite.

J. R. P.

**Transference Numbers of Sodium and Potassium in Mixed Chloride Solutions.** S. A. BRALEY and J. LOWE HALL (*J. Amer. Chem. Soc.*, 1920, **42**, 1770—1776).—

Over a range of total concentration from 0.2*N* to 1.6*N* with equivalent amounts of sodium and potassium chlorides, a relatively greater amount of sodium is transferred than is indicated by calculation from the conductance of the simple salt solutions, on the basis of the iso-

hydric principle. The increase of sodium transferred over this range of concentration is, roughly, a linear function of the total salt concentration. The results are in harmony with those of Smith and Ball (A., 1917, ii, 247), and may be explained on the basis of complex formation, the simplest form of which may be expressed in the form  $\text{NaCl} + \text{KCl} \rightleftharpoons \text{Na}(\text{KCl}_2) \rightarrow \text{Na}^+ + \text{KCl}'_2$ .

J. R. P.

**Dependence of Electro-osmosis on the Chemical Properties of the Diaphragm.** STANISLAW GLIXELLI (*Anzeiger Akad. Wiss. Krakau*, 1917, [A], 102—128; from *Chem. Zentr.*, 1920, iii, 431).—The fundamental assumption in the theory of electro-osmosis is that the potential of the mobile layer of liquid,  $\phi_1$ , differs from the potential,  $\phi_0$ , of the layer attached to the wall of the diaphragm. A proportionality exists between the difference of potential ( $\phi_1 - \phi_0$ ) of the electrical double layer and the rate of electro-osmosis or cataphoresis. The causes of the difference of potential and the mechanism of the phenomenon of the charge in the electrical double layer are discussed. All that is known is that the electrical double layer is considerably influenced by the addition of electrolytes, more particularly by hydrogen and multi-valent ions and by the cations of the heavy metals and complex organic bases, and that the positively charged diaphragms are discharged by anions and the negatively charged ones by cations. The methods previously adopted have not permitted the use of moderately concentrated electrolytes. The author has elaborated a method of observing and approximately measuring the velocity of electro-osmosis which is particularly adapted to the estimation of the isoelectric point; it can be used with gels and powders, and permits the employment of approximately 0.5*N*-solutions of electrolytes. The influence of hydrogen and hydroxyl ions on the electric charge of the following inorganic gels has been examined: silicic and tungstic acids, antimonie anhydride, stannic and titanate acids, glucinum oxide and hydroxide, zinc, iron, magnesium, and silver oxides, and nickel hydroxide. With some of these, the concentration of hydrogen and hydroxyl ions at the isoelectric point is determined; with others, the lower limit of its value is ascertained. With regard to the hydrogen-ion concentration at the isoelectric point, the substances examined fall into four distinct groups: acids, acid ampholytes, basic ampholytes, and bases. The results of the investigation are examined in the light of the present theories of the origin of the electric charge in colloid particles.

H. W.

**Specific Heat of Liquids at Constant Volume.** K. ZAKRZEWSKI (*Anzeiger Akad. Wiss. Krakau*, 1917, [A], 86—101; from *Chem. Zentr.*, 1920, iii, 440).—The values for  $(\partial p / \partial t)_v = \alpha / \mu$  are calculated from the measurements of Seitz and Lechner (A., 1916, ii, 174). Whilst these values for ethyl alcohol at different temperatures between 0° and -90° lie with sufficient accuracy on a straight line in the  $\partial p / \partial t$  volume diagram, for

ethyl ether and carbon disulphide they lie on different lines which are parallel to one another. Within this interval,  $\partial^2 p / \partial t^2 = 0$  for alcohol, and therefore  $c_v$  is independent of the volume. For ether and carbon disulphide, on the other hand,  $(\partial p / \partial t)_v = A + Bv$ , in which  $A$  is a function of the temperature, and hence  $\partial c_v / \partial v = T \partial^2 p / \partial t^2 = T \partial A / \partial t$ . Since the dependence of the specific heats,  $c_p$ , of these liquids on temperature has been investigated in this region by Battelli, it is possible to calculate  $c_v$  (for a mean volume,  $v$ ). The following values for this factor are thus obtained:

	0°.	- 20°.	- 30°.	- 50°.	- 70°.	- 90°.
Ethyl alcohol.....	—	—	0.406	0.386	0.370	0.358
Ethyl ether .....	—	0.397	—	0.386	0.376	0.362
Carbon disulphide ...	0.160	0.139	—	0.121	0.114	0.110

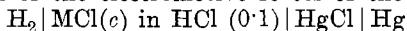
A bend such as would be expected from the Planck-Einstein formula is only observed in the case of ether when  $c_v$  is plotted against the temperature; the opposite bend observed with alcohol and carbon disulphide is attributed by the author to the existence of complex molecules in these liquids. H. W.

**Thermodynamics of Chemical Equilibrium in Condensed Mixtures.** H. CASSEL (*Zeitsch. Physik*, 1920, 2, 71—75).—This is a straightforward thermodynamic argument, apparently proving rigorously, from Planck's statement of the third law, that any difference between the specific heats of the mixture and of the components separately, or any thermal effect on mixing, or any curvature in the vapour pressure isotherms, is a sign of chemical action. The effect of volume changes or deviations of the vapour from the gas laws is neglected, however. CHEMICAL ABSTRACTS.

**Thermodynamic Properties of the Ions of some Strong Electrolytes and of the Hydrogen Ion in Solutions of Tenth-Molal Hydrochloric Acid containing Univalent Salts.**

HERBERT S. HARNED (*J. Amer. Chem. Soc.*, 1920, 42, 1808—1832).

—Measurements of the electromotive forces of the cells



at 18°, 25°, and 30°, containing potassium, sodium, and lithium chlorides, respectively, have been made. Assuming the complete dissociation of the above electrolytes, it is shown that the hypothesis of the individual ion activities as postulated by MacInnes (A., 1919, ii, 385) is true within narrow limits, and that at a given concentration of potassium chloride the potassium and chlorine ion activities are identical within narrow limits. The individual ion activity-coefficients of the hydrogen, potassium, sodium, lithium, and chlorine ions from concentrations 0.1 to 3M have been calculated.

It is shown that the semi-empirical formula  $\log F_a = \alpha c - \beta c^m$ , where  $F_a$  is the activity-coefficient of the ion,  $c$  the concentration, and  $\alpha$ ,  $\beta$ , and  $m$  are constants, will express  $F_a$  as a function of  $c$  within experimental error from 0.01 to 3M concentration. A table



of the free energies and heat content decreases of the cell reaction  $\text{H}_2 + 2\text{HgCl} = 2\text{HCl}(0.1) + 2\text{Hg}$  in the presence of potassium, sodium, and lithium chlorides, respectively, has been compiled.

On the assumption that the ions have independent heat contents of transfer, and that at a given concentration of potassium chloride the potassium and chlorine ions possess identical heat contents of transfer from a solution of concentration  $c_1$  to a solution of concentration  $c_2$ , it is possible to calculate the decrease of heat content of transfer of the hydrogen ion from solutions of  $\text{MCl}(c)$  in  $\text{HCl}(0.1)$  to  $\text{HCl}(0.1)$ . The results are tabulated. This decrease is shown to be a function of the total ion activity of the solution, not of the activity of the hydrogen ion.

J. R. P.

**Equation of State Covering all States of Aggregation and the Law of Action of the Molecules.** LEON SCHAMES (*Zeitsch. Physik*, 1920, 1, 376—384).—The author derives values for some of the constants of his equation.

CHEMICAL ABSTRACTS.

**Melting-point Methods at High Temperatures.** LEO I. DANA and PAUL D. FOOTE (*Trans. Faraday Soc.*, 1920, 15, 186—217).—Detailed descriptions are given of the methods of determining the melting points of metals, inorganic salts, and silicates by means of thermocouples, resistance thermometers, and optical pyrometers, as well as special methods. The following melting points are recorded: tin,  $231.9^\circ$ ; bismuth,  $271^\circ$ ; cadmium,  $320.9^\circ$ ; lead,  $327.4^\circ$ ; zinc,  $419.4^\circ$ ; antimony,  $630.0^\circ$ ; aluminium,  $658.7^\circ$ ; silver,  $960.5^\circ$ ; gold,  $1063.0^\circ$ ; copper,  $1083.0^\circ$ ; nickel,  $1452^\circ$ ; cobalt,  $1480^\circ$ ; iron,  $1530^\circ$ ; palladium,  $1550^\circ$ ; chromium,  $1615^\circ$ ; platinum,  $1755^\circ$ ; silicon,  $1420^\circ$ ; sodium molybdate,  $687^\circ$ ; borax,  $741^\circ$ ; sodium chloride,  $801^\circ$ ; sodium sulphate,  $884^\circ$ ; sodium metasilicate ( $\text{Na}_2\text{SiO}_3$ ),  $1088^\circ$ ; lithium metasilicate,  $1202^\circ$ ; lithium orthosilicate ( $\text{Li}_4\text{SiO}_4$ ),  $1255^\circ$ , and various silicates, aluminates, and refractory materials.

J. R. P.

**The Relation between Boiling Point in the Vacuum of the Cathode Light and Critical Temperature.** P. WALDEN (*Zeitsch. anorg. Chem.*, 1920, 112, 225—232).—Making use of the data given by Krafft (A., 1896, ii, 464; 1899, ii, 464) for a number of paraffins, fatty acids and their esters, and benzene homologues of high molecular weight, it is shown that the ratio of the absolute boiling point,  $T_{15}$  at 15 mm., to that,  $T_0$ , in the vacuum of the cathode rays, has a mean value of 1.2. The ratio between the boiling points at 15 mm. and 760 mm. is given by  $T_{15}/T_{760} = 0.765$ . It follows that  $T_{760}/T_0 = 1.59$ , which is identical with the mean experimental value for the higher paraffins. This value is practically identical with that found by van Laar for the ratio of the critical temperature to the boiling temperature at atmospheric pressure,  $T_k/T_{760} = 1.60$ . Hence the critical temperature is 2.54 times the boiling temperature in the highest vacuum. In the case of the metals potassium, sodium, silver, and copper, the relation between  $T_{760}$  and  $T_0$  is expressed by  $T_{760} = 4.55T_0/\log T_0$ .

The above relation between critical temperature and boiling points is applied to calculate the critical temperature of metals. For those metals of which the boiling point in absolute vacuum is not known, this is calculated from the relation that  $T_0/T_{\text{vap.}} = 1.8$ , where  $T_{\text{vap.}}$  is the temperature at which vaporisation begins in the vacuum of the cathode rays.

E. H. R.

### Direct Measurement of the Thermal Molecular Velocity.

OTTO STERN (*Zeitsch. Physik*, 1920, **2**, 49—56).—A silvered platinum wire is electrically heated in a high vacuum (0.0001 mm. Hg) until silver molecules leave it with a mean free path greater than the length of the containing vessel. Those of a certain direction are selected by passing two slits 0.2 mm. wide, and next strike a brass screen 10 cm. away, where they condense as a dark line. If the apparatus is rotated, the line is displaced by an amount from which the velocity of the molecules can be calculated. The speed of rotation was 1500 rev. per minute, and the displacement about 4 mm. The indirectly known value was confirmed to 15%, about the uncertainty due to imperfect knowledge of the temperature. The molecule of gaseous silver was shown to be monatomic.

CHEMICAL ABSTRACTS.

**Determination of Vapour Pressure.** E. J. HARTUNG (*Trans. Faraday Soc.*, 1920, **15**, 150—159).—An improved tensimeter is described, which allows of the determination of vapour pressures with great accuracy. The vapour pressures at 0° of solutions of potassium chloride, potassium sulphate, and sulphuric acid were compared with that of a solution of potassium chloride saturated at 0°.

J. R. P.

### Vapour Pressure of Aqueous Solutions of Mannitol.

J. C. W. FRAZER, B. F. LOVELACE, and T. H. ROGERS (*J. Amer. Chem. Soc.*, 1920, **42**, 1793—1808).—The vapour pressure lowerings of aqueous mannitol solutions have been determined over the range of solubility of the substance. The error due to dissolved air was eliminated. A mean deviation from Raoult's law of only 0.0006 mm. was found up to 0.8 molar concentration. By comparison with freezing-point lowerings, it is found that  $\log_e p_0/p_1$  decreases with the temperature, or the heat of dilution has a small negative value for concentrations up to 0.5 molar. Comparisons with boiling-point determinations show that this changes to a positive value at higher concentrations.

J. R. P.

### Thermochemistry of Ionisation of Vapours of certain Compounds.

PAUL D. FOOTE and F. L. MOHLER (*J. Washington Acad. Sci.*, 1920, **10**, 435—444).—If a material in the vapour state ionises by dissociation it is sometimes possible to calculate the ionisation potential from chemical and physical data. In the case of alkali-metal haloids, all the necessary data are known except the heat of sublimation. The heat of sublimation may be calculated

for haloids of metals of the second group from the vapour pressures. The ionisation potentials are computed for hydrogen chloride, bromide, iodide and sulphide, and the value for hydrogen chloride is found to be in agreement with the number determined by the authors.

J. R. P.

**Thermochemistry of Carbon Compounds.** A. THIEL (*Ber.*, 1920, **53**, [B], 1378—1382).—A criticism of the work of Fajans (this vol., ii, 354) and von Steiger (this vol., ii, 355). The author considers that Fajans' calculations are to some extent based on fundamentally invalid assumptions. For example, the existence of monatomic carbon vapour is assumed into which carbon could only dissociate to the extent of about 50% at 10,000° according to calculations based on the theory itself. It is further assumed that the atoms in the crystal lattice of diamond are united to one another by the same valencies as in aliphatic compounds. In general, however, this can scarcely be the case, since it would then be impossible to explain the crystalline form of elements of lower valency; in all probability, only subsidiary valencies can be involved.

H. W.

**The Benzene [Formula] Problem. III.** A. VON WEINBERG (*Ber.*, 1920, **53**, [B], 1353—1358).—As a result of recent experiments, Debye and Scherrer (*A.*, 1917, ii, 437) have been led to the conclusion that carbon in the form of diamond is to be regarded as the prototype of aliphatic compounds, whilst graphite and amorphous carbon are the simplest stages in aromatic chemistry. The author does not regard the production of mellitic acid from graphite (and not from diamond) as valid evidence of aromatic nature, since it is not a primary product. Further, Debye and Scherrer have seen in the suppressed fourth valency of the carbon atoms in benzene an analogy to the mechanically suppressible fourth valency of the graphitic carbon atom, and point to the behaviour of the triarylmethyls as proof of the existence of such weakened fourth valencies; in reality, however, the valency is not weakened, as is evidenced by the behaviour of this class of substance towards oxygen, but only intermittently saturated in consequence of the induced vibrations of the central carbon atom. Von Steiger (this vol., ii, 355) has adduced evidence in favour of Debye and Scherrer's hypothesis by consideration of the heats of combustion of aromatic compounds. It is shown, however, that the energy involved in the isolation and combustion of a carbon atom in benzene is 5.3 Cal. greater than that involved in the case of an aliphatic hydrocarbon and 7 Cal. greater than that involved with graphite. It therefore appears that benzene rings cannot be present in graphite, and, more generally, that it represents a particular type of union. The kinetic formula for benzene leads to the hypothesis that the excess of energy (5.3 Cal.) for an aromatic in comparison with an aliphatic carbon atom is a consequence of its more rapid movement, and is the logical conclusion of the theory that the energy excess of

multiple bonds is kinetic in origin—a theory which is defended by examples against the criticisms of Fajans. H. W.

### Heats of Combustion and Energy of Dissociation. I.

A. VON WEINBERG (*Ber.*, 1920, **53**, [B], 1347—1353).—The present communication contains a concise statement and justification of the views previously expressed in part by the author (this vol., ii, 14) and more recently criticised in some particulars by Fajans (this vol., ii, 354). They may be expressed in the following manner: (1) in saturated aliphatic hydrocarbons, the energy of dissociation of a C—C bond is equal to that of a C—H bond, that is,  $Q_{CC} = Q_{CH}$ ; (2) the absolute value of  $Q_{CH}$  is 7.5 Cal. greater than the energy of dissociation of a hydrogen molecule; (3) molecular cohesive forces have not to be overcome in the combustion of solid carbon, which practically only requires the provision of the energy of four C valencies for the carbon atom. The absolute value for diamond or graphite is  $2Q_{CC} + 1.5$  Cal. (4) In the oxidation of carbon monoxide to carbon dioxide the energy of dissociation of the two so-called unsaturated valencies is equal to  $Q_{CC}$ .

(1) If it be admitted that the energy required for the separation of two similar or dissimilar atoms is evenly distributed between the atoms, the following expression is obtained for the energy of disruption of a hydrocarbon,  $C_nH_{2n+2} - [(n-1)Q_{CC} + 2n + 2/2 \cdot Q_{CH}] - [2n + 2/2 \cdot Q_{CH}]$ , in which the left bracket represents the energy required for the separation of  $n$  carbon atoms and the right bracket that required for  $2n + 2$  hydrogen atoms. The contribution of the  $n$  carbon atoms towards the heat of combustion of the hydrocarbon is  $nx = -[(n-1)Q_{CC} + (n+1)Q_{CH}] + nQ_{CO_2} - nQ_{O_2}$ , where  $Q_{CO_2}$  and  $Q_{O_2}$  are the energies of dissociation of carbon dioxide and oxygen. The summation law demands that this shall be true for any value of  $n$ , which can only be the case when  $Q_{CC} = Q_{CH}$ . (2) The values for the energy of dissociation of a hydrogen molecule are calculated from the recent experiments of Franck, Knipping, and Krüger. It is at present impossible to elucidate the intramolecular process on which the difference depends. (3) If 96 Cal. be adopted as the most probable value for the heat of combustion of solid amorphous carbon, it appears that the latter behaves during combustion as a gaseous saturated hydrocarbon. Solid carbon therefore occupies a position different from that of all solid organic compounds, and it appears justifiable to conclude that liquid molecular carbon is incapable of existence. The heat of combustion of diamond has been determined with great accuracy to be 94.5 Cal., and this difference of 1.5 Cal. can only be explained on the supposition that the work of dissociation in diamond is correspondingly greater. (4) Thomsen has already endeavoured to calculate the absolute value for the energy of dissociation of a carbon atom from solid carbon by consideration of the oxidations of the element to carbon monoxide and dioxide respectively, but the author holds this mode of reasoning to be incorrect, since it assumes the similarity of the C—O double bond in carbon monoxide and the two C—O linkings in carbon dioxide.

He prefers to calculate  $Q_{CO}$  from the heats of combustion of a number of aldehydes and ketones, and thus deduces the value 66.7 Cal. (the value may be slightly inaccurate on account of the experimental difficulties in working with the more volatile substances); the mean value of the heat of combustion of carbon monoxide as determined by Berthelot and Thomsen is 67.4 Cal., a figure which agrees with the former within the limits of experimental error. It follows, therefore, that the two so-called unsaturated valencies of carbon monoxide are not free during combustion, but require as much energy for their separation as does the carbonyl group of a ketone. It therefore seems probable that the four carbon valencies in carbon monoxide are attached to the oxygen atom.

H. W.

### Heats of Combustion and Energy of Dissociation. II.

A. VON WEINBERG (*Ber.*, 1920, **53**, [B], 1519—1528).—On the basis of the ideas developed in previous communications (this vol., ii, 14, and preceding abstract), the author has calculated the energy necessary for the fission of the commoner atomic linkings in organic compounds. In the following, the energy of dissociation is represented by  $Q$ , and the index shows the linking concerned.

It is found that  $Q_{CC} = Q_{CH} = Q_{C-O} = Q_{NH} = Q_{N-N}$ , or that five of the commonest linkings in organic compounds are almost equally stable at 18°. The elimination of the first oxygen atom from carbon dioxide requires an expenditure of energy equal to 126.7 Cal., whilst for the second oxygen atom 265.5 Cal. (approximately double that used in the former case) are necessary.  $Q_{O-H}$  in ethyl alcohol and ethylene glycol is calculated to be 96.8 and 98.7 Cal. respectively, whilst in water it is 99.2 Cal.; the difference lies within the limits of experimental error, but it is quite possible that the OH linking in alcohols is slightly less stable than in water. The values calculated for  $Q_{N\equiv N}$  and  $Q_{NC}$  are 266.4 Cal. and 233.1 Cal.; from this it follows that the treble bond in the case of nitrogen, in contrast to that of carbon, is exactly equivalent to three single bonds, and this explains why substances containing the group  $C\equiv N$  or  $N\equiv N$  are not possessed of the same lability and power of forming additive compounds as are those containing the  $C:C$  group.  $Q_{NC}$  and  $Q_{NC_2}$  are 170.9 Cal. and 243.7 Cal. respectively.  $Q_{HCl}$  is calculated to 119.2 Cal., which is in good agreement with the value (119 Cal.) found by Born (this vol., ii, 156) by a totally different method, and thus strikingly confirming Born and Haber's prediction that the energy of dissociation,  $Q_{HCl}$ , is equal to the electronic affinity of the chlorine atom.  $Q_{CCl}$  is calculated to be 119.6 Cal., so that practically the same expenditure of energy is necessary to separate the hydrogen nucleus from the electron, the hydrogen atom from the chlorine atom, and the latter from the carbon atom.  $Q_{Cl-O}$ ,  $Q_{HBr}$ ,  $Q_{CBr}$ ,  $Q_{HI}$  and  $Q_{CI}$  are 78.8, 76.3, 74.2, 59.4, and 54.5 Cal. respectively, so that bromine and iodine are rather more firmly combined with hydrogen than with carbon. The equality of energy of dissociation and electronic affinity is not found with bromine and iodine. The difference between the energy of the corresponding linkings explains the differ-

ences in the reactivity of the alkyl haloids.  $Q_{S_2}$  is calculated to be 104.5 Cal., which is in good agreement with the value (103.6 Cal.) determined experimentally by Budde.  $Q_{SO_2}$  and  $Q_{SO_3}$  are respectively 254.5 Cal. and 336.2 Cal.;  $Q_{CS}$  and  $Q_{H_2S}$  are 73.1 Cal. and 152.8 Cal. respectively (the latter value differing widely from that calculated by Born). For  $Q_{SOCl}$  the values 76.4 Cal. and 71.2 Cal. are calculated from different compounds.

H. W.

**Heat of Oxidation of Glucinum.** H. COPAUX and CH. PHILIPS (*Compt. rend.*, 1920, 171, 630—632).—From measurements of the heat of solution of glucinum and its oxide respectively in hydrofluoric acid the author calculates the heat of oxidation of glucinum to be given by  $Gl_{sol.} + O_{gas} = GlO_{sol.} + 151.5 \text{ cal.}$

W. G.

**Physico-chemical Properties of Highly Concentrated Dispersoidal Solutions of Noble Metals.** N. I. MOROSOV (*J. Russ. Phys. Chem. Soc.*, 1915, 47, 783).—The viscosity of a 17.7% silver solution at 19.5° is 1.1129 times that of water. The viscosity decreases with increasing temperature, for example, the time of flow for 17.7% silver solution at 19.5° is 49.7 sec. and at 34.5°, 37 sec. The study of dispersoidal solutions (viscosity, b. p., etc.) of high concentrations undoubtedly will make possible a qualitative correlation among the degree of dispersity, the concentration of disperse phase and changes of properties of the disperse medium.

CHEMICAL ABSTRACTS.

**The Viscosity of Liquids. IV. Ideal Mixtures of the Types Ether-Ether and Ester-Ester.** JAMES KENDALL and ALEXANDER HOLLAND WRIGHT (*J. Amer. Chem. Soc.*, 1920, 42, 1776—1784. Compare A., 1914, ii, 109; 1917, ii, 524, 525).—The viscosity curves for the following liquid systems have been determined with the use of the Bingham viscosimeter: (1) ethyl ether-phenetole; (2) ethyl ether-diphenyl ether; (3) phenetole-diphenyl ether; (4) ethyl acetate-ethyl benzoate; (5) ethyl acetate-benzyl benzoate; (6) ethyl benzoate-benzyl benzoate. Although these mixtures are certainly very nearly ideal, yet the experimental data are not reproducible satisfactorily by means of any known simple formula. The logarithmic viscosity formula of Arrhenius gives values uniformly a little low; the cube root viscosity equation of Kendall and Monroe (*loc. cit.*) gives values uniformly a little high. All other proposed formulæ are altogether out of agreement with the figures of experiment. It is concluded that the experimental work has advanced as far as possible, and that further progress must be preceded by fundamental advances in the theory of the subject.

J. R. P.

**The Influence of Temperature on the Surface Tension of Narcotics.** HANS WINTERSTEIN [with (FRL.) ELSE HIRSCHBERG] (*Biochem. Zeitsch.*, 1919, 100, 81—83).—The surface activity of benzamide, monacetin, salicylamide, and ethyl urethane increases with a rise in temperature.

S. S. Z.

**The Influence of Hydrogen Sulphide on the Occlusion of Hydrogen by Palladium. II.** EDWARD BRADFORD MAXTED (T., 1920, 117, 1280—1288).

**Adsorption from Solutions of Substances of Limited Solubility.** M. POLÁNYI (*Zeitsch. Physik*, 1920, 2, 111—116).—  
A mathematical paper. CHEMICAL ABSTRACTS.

**Mechanism of the Surface Phenomena of Flotation.** IRVING LANGMUIR (*Trans. Faraday Soc.*, 1920, 16, 62—74).—The adsorption of organic substances with large molecules originates from certain atoms in the molecule. Wetting is due to the attraction between the material wetted and some active group in the liquid molecule. A study of cleaned and oiled glass surfaces showed that films of molecular thickness are sufficient to alter radically the surfaces of solids, both as regards the lubricating properties of these films and the contact angles made by water drops. The formation of froth depends on the presence of substances which can form a stable unimolecular film over the surface of each bubble. In order that a froth may readily form, it seems desirable to have present a soluble substance having a strong tendency to be adsorbed on the surface of the liquid. The presence of alkalis in flotation is to be avoided, probably because the hydroxyl ion tends to draw the carboxyl group of the fatty acid to itself rather than allow it to attach itself to the solid particles. The tendency of particles to attach themselves to bubbles of the froth is measured by the contact angle formed between the oily surface of the bubble and the contaminated surface of the solid. The selective action by which substances like galena are separated from quartz and calcite is dependent on the contact angle formed by the oiled surfaces rather than on any selective tendency for the oil to be taken up by some minerals more than by others. J. R. P.

**The Diffusion of Electrolytes into Jellies. III. The Relation of the Distance of Diffusion to the Diffusion Coefficient and its Dependence on the Concentration of the Indicators.** OTTO FÜRTH, HANS BAUER, and HANSI PIESCH (*Biochem. Zeitsch.*, 1919, 100, 29—64. See A., 1919, ii, 13; this vol., ii, 94).—The diffusion of various electrolytes in agar jellies was studied, and it was found that the laws of diffusion could also mostly be applied to diffusion into jellies. It was further found that the "invasion factor," that is, the relation of the distance of diffusion of the electrolyte in question to that of a sodium chloride solution of the same molecular concentration diffusing under the same conditions, was an approximate measure for the square root of the diffusion-coefficient. It is concluded from this that most electrolytes also penetrate jellies according to the mobility of their ions providing that chemical affinity and colloidal changes do not interfere. The

distance of diffusion is influenced by the concentration of the indicator in the jellies. S. S. Z.

**The Effect of Asymmetry. A Study in Crystal Structure.**

THOMAS VIPOND BARKER and MARY WINEARLS PORTER (T., 1920, 117, 1303—1321).

**The Electrochemical Behaviour of Mixed Crystals of Gold with Copper and Silver.** G. TAMMANN (*Zeitsch. anorg. Chem.*, 1920, 112, 233—243).—In previous papers (A., 1919, ii, 398, 406) it has been shown that there is a limiting composition for gold-copper and gold-silver alloys, such that, when the gold content exceeds this limit, the alloys are not attacked by different chemical reagents. The limiting composition was correlated with the probable distribution of the two kinds of atom on a face-centred cubic lattice in the crystalline structure of the alloy. The electrochemical properties of these alloys have now been investigated. When copper-gold alloys are used as anode in an electrolytic cell, with a copper cathode and copper sulphate or nitrate as electrolyte, the limiting composition is about 0.27 to 0.30 mol. of gold; with a smaller proportion of gold than this, copper is dissolved from the anode. With gold-silver alloys as anode, using sulphuric or nitric acid as electrolyte, the limiting composition is 0.35 to 0.40 mol. of gold. Similar limits were found when the decomposition potentials of such cells were measured. On the other hand, to obtain a persistent polarisation effect of 1.4 volts in the case of gold-copper and 0.73 volt for gold-silver, the proportion of gold to silver or copper must not fall below 0.5 mol. The normal limiting composition for weak oxidising agents, such as hydrogen peroxide, in acid or alkaline solution is about 0.25 mol. of gold; in the case of anodic oxygen, therefore, this normal limit is exceeded. The same is true of anodic sulphur, produced by the electrolysis of sodium sulphide, the limit in this case being more than 0.50 mol. of gold.

Discussing these observations from the point of view of the space-lattice theory, the author points out that in an alloy containing 0.25 mol. of gold, that is, 1 atom of gold to 3 of copper, in the face-centred cubic lattice there will not be in any cube face plane any two copper atoms the distance of which from one another corresponds with the minimum translation in the lattice. The alloy would therefore be protected against attack by any agent which needs two atoms of copper. If the agent can attack the copper, on the outer planes, but the gold atoms retain their positions, then, if the agent cannot penetrate the structure, the alloy is still resistant.

The limiting composition for strong anodic polarisation of the alloys, 0.5 mol. gold, is the same as the limiting composition in gold-palladium alloys for hydrogen solubility. These facts may be correlated with the presence in the structure of alloys containing 0.5 mol. of gold or less of cube edges or diagonals formed exclusively of copper or silver or palladium atoms. E. H. R.



**Relation between the Solubilities of Solutes and their Molecular Volumes.** SHINKICHI HORIBA (*Trans. Faraday Soc.*, 1920, **15**, 178—185).—When a solute of molecular volume  $V$  is dissolved in a solvent of molecular volume  $v$ , the number of molecules of solvent which can surround one solute molecule is approximately  $4/1.1 \cdot (\sqrt[3]{V/v} + 1)^2$ , assuming that  $V$  is distinctly larger than  $v$ . If the logarithms of the solubilities are plotted against this expression, straight lines are obtained. J. R. P.

**Mutual Action of Trimethylsulphanilic Acid and Strong Electrolytes.** MASAO KATAYAMA and NOBUO YAMADA (*J. Tokyo Chem. Soc.*, 1920, **41**, 193—224).—It has been shown (*ibid.*, **36**, 745) that trimethylsulphanilic acid is not an electrolyte, but lowers the electrical conductivity of other electrolytes, due either to interference of ionic velocity of the electrolytes or to formation of complex salts. The authors failed to obtain the crystalline complex salts reported by Griess (*A.*, 1880, 322), except when potassium salts were present. The complex salts prepared by Griess, therefore, must have either contained potassium salts or methylation must have been incomplete. From determinations of the transport number of hydrochloric acid containing the sulphonic acid, it is shown that there is no complex salt formation. Viscosity measurements of aqueous solutions of trimethylsulphanilic, hydrochloric, and acetic acids show that the effect is additive for acetic acid and the sulphonic acid, but is not so for hydrochloric acid and the sulphonic acid. The change of conductivity of both hydrochloric and acetic acids produced by the addition of the sulphonic acid is entirely due to the change of viscosity. The solubility and the change of volume produced when the sulphonic acid is added to water, hydrochloric acid, and acetic acid are also measured. The general conclusion is that hydrochloric acid increases the dissociation of trimethylsulphanilic acid, but the latter does not affect the dissociation of hydrochloric acid. CHEMICAL ABSTRACTS.

**Reversible and Irreversible Dispersoidal Parasitism.** P. P. VON WEIMARN, N. I. MOROSOV, and V. J. ANOSSOV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 782).—An investigation on the conditions of formation of dry and solid preparations of silver, which are reversibly soluble, leads to the following conclusions: Dispersoidal parasitism is reversible in the limits of ordinary temperature (20—25°) only when the substance which originates it is soluble at these temperatures. Examples: silver + gum, silver + dextrin. Dispersoidal parasitism is irreversible in the limits of the ordinary temperature if the substance which originates it is insoluble at these temperatures. Examples: silver + agar, silver + gelatin. Gelatin and agar are therefore stabilisers only for liquid preparations of dispersoidal silver, and the dried preparations do not dissolve in water at 20—25°. A method has been developed for obtaining liquid solutions of silver of very high dispersity; concentrations of 15% and more are easily obtainable in about one hour. CHEMICAL ABSTRACTS.

**Method of obtaining Dry Precipitates of any Insoluble Substances, which pass into Dispersoidal-dissolved State Commencing only from some Fixed Temperatures.** P. P. von WEIMARN, N. I. MOROSOV, and V. J. ANOSSOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 197).—Dispersoidal parasitism is characterised by the fact that any insoluble substance (for example, silver, sulphur, barium sulphate, etc.) receives nearly the same properties of "solubility" as a substance at the expense of which it parasites. Therefore, by mixing together any insoluble precipitate of high dispersity with various substances which are parasitised and which are sufficiently soluble, for example, successively at 10°, 20°, 30°, 40°, etc., there is obtained a succession of dry preparations of the insoluble substance. These preparations are "soluble" also successively in the vicinity of temperatures enumerated above. Many organic substances (solutoids, for example, gelatin), on heating of their solutions for a long time, give products soluble at still lower temperatures than the original substance. These temperatures are lower the longer the solution is heated. These products are especially convenient for realisation of the method here described. For example, a dry precipitate of dispersoidal silver (63% of Ag) which is prepared with gelatin, previously boiled for seven hours, practically "does not dissolve" in water at about 20°, but it "dissolves" excellently at about 35°, giving very stable silver "solutions" of high dispersity. CHEMICAL ABSTRACTS.

**Coagulation of Agar-agar Hydrosol.** KEIZO IWASE (*J. Tokyo Chem. Soc.*, 1920, **41**, 468—479).—The effects of temperature and of salts on the velocity of coagulation were studied. Agar-agar was washed with dilute acetic acid, water, aqueous ammonia, and water, dissolved by heat, and then filtered. The precipitate produced by alcohol, and dried with alcohol and ether, was a white powder. A known concentration of agar-agar was prepared by dissolving this powder and heating under a reflux condenser. The hydrosol thus obtained was transferred to test-tubes and kept in a bath 20° higher than the temperature under which experiments were to be conducted. The end-point of the coagulation was taken at the time when the agar not only would not flow, but also its surface meniscus could not be disturbed on inverting the test-tube. The general conclusions are: The more concentrated the hydrosol, the greater is the speed of coagulation. The effect of the salts on coagulation time is greater when the hydrosol is the more concentrated. Series of ionic effect are  $K > Na, SO_4 > CH_3 \cdot COO > C_6H_4O_5 > Cl > Br > NO_3 > I$ . Although the temperature effect on the speed of coagulation is very great, the order of this series of the salt effect at different temperatures does not change. The heating of the sol prolongs the time of coagulation, finally rendering it non-coagulable. CHEMICAL ABSTRACTS.

**Sedimentation.** PETER RONA and PAUL GYÖRGY (*Biochem. Zeitsch.*, 1920, **105**, 133—140).—According to Bodländer (*Jahrb. Min.*, 1893, **2**, 147), small proportions of electrolytes

soluble in water cause rapid clarification of kaolin suspensions, whereas soluble non-electrolytes, even in large amounts, are ineffective in this respect (compare Kruyt and van Duin, A., 1914, ii, 182; Freundlich and Rona, A., 1917, ii, 365; Rona and Michaelis, A., 1919, ii, 269). The authors have now made further experiments with methyl, ethyl, isopropyl, amyl, heptyl, *n*- and *sec*-octyl, and decyl alcohols, methyl-, ethyl-, propyl-, isobutyl-, and phenyl-urethanes, diphenylthiocarbamide, chloroform, tributyrin, camphor, and thymol, and find that nearly all of these non-electrolytes increase the velocity of sedimentation of kaolin. In homologous series, this acceleration increases in magnitude with the length of the chain, and only with compounds virtually insoluble in water is no effect detectable.

The increases in the viscosity of water produced by these compounds are at most very small, and the authors assume that the non-electrolytes produce a sensibilisation of the suspended particles towards the electrolytes always present, and thus increase the velocity of sedimentation of the kaolin particles. This view is supported by the observation that the velocity of sedimentation of charcoal is not influenced by non-electrolytes. T. H. P.

**Structure of Precipitates.** SVEN ODÉN (*Svensk. Kem. Tidskr.*, 1920, 32, 90—98; from *Chem. Zentr.*, 1920, iii, 326—327. Compare this vol., ii, 600).—The author has endeavoured to develop a theory concerning disaggregation and aggregation with increasing electrolyte content, but the subject is difficult, on account of the limited knowledge regarding the electrical double layer. Freundler's absorption formula may be adopted, and the assumption may be made that for each type of ion a special adsorption isotherm of the form  $y = \beta c^a$  exists in which the coefficient is greater for one variety of ion and the exponent greater for the other. The derived relationships are expressed by graphs. The author considers that the so-called peptisation of a precipitate consists exclusively in the adsorption of ions, with discharge of the primary particles and subsequent scattering of the aggregates. The influence of concentration, temperature, and rate of admixture of the reacting solutions on the size of the primary particles has been accurately investigated. The effect of concentration on the structure of precipitated barium sulphate has been examined with solutions of barium thiocyanate and ammonium sulphate. If the concentration of the supersaturated barium sulphate solution at the moment when primary particles separate be denoted by  $M$ , it appears that, with diminishing concentration of the reacting solutions, the primary particles are of sufficient size to remain stable when  $M = 0.25$ . The distribution curves for the magnitudes of the particles are given. If one solution is added drop by drop to the other, the barium sulphate primarily formed separates at a considerably lower value of  $M$ , and consequently in correspondingly larger particles than if the total quantity of barium sulphate is simultaneously produced. The influence of rate of addition on the primary structure is quantitatively examined with the help of

solutions of barium nitrate and ammonium sulphate, and the results are given in a series of graphs. Finally, the effect of temperature is studied, and the well-known phenomenon that precipitated barium sulphate becomes coarser with increasing temperature is quantitatively examined. H. W.

**Copper Ferrocyanide.** E. J. HARTUNG (*Trans. Faraday Soc.*, 1920, **15**, 160—177).—Preliminary experiments on the equilibrium between moist copper ferrocyanide and aqueous vapour, and on the adsorption of potassium chloride and potassium sulphate from solutions by copper ferrocyanide, are described. The function of copper ferrocyanide in semi-permeable membranes is discussed.

J. R. P.

**Equation for the Chemical Equilibrium of Homogeneous Mixtures.** ALFRED W. PORTER (*Trans. Faraday Soc.*, 1920, **15**, 75—82).—A mathematical paper in which the conditions for the equilibrium of a homogeneous mixture at constant temperature, and the effect of pressure on the equilibrium constant, are deduced by rigorous methods.

J. R. P.

**Self-ignition of Ethyl Ether-Air Mixtures.** J. A. MCCLELLAND and H. V. GILL (*Sci. Proc. Roy. Dublin Soc.*, 1920, [N.S.], **16**, 109—119).—Ignition occurs when a mixture of ethyl ether vapour and air is allowed to rush into a partly exhausted tube. Measurements of the temperature in the tube showed that the rise of temperature produced reached the ignition point of the mixture. The rise of temperature is attributed to the conversion into heat of the translational energy of the gas rushing into the tube. The length of the explosion tube affects the results. J. R. P.

**Theory of Velocity of Reaction.** M. POLÁNYI (*Zeitsch. Physik*, 1920, **2**, 90—110. Compare this vol., ii, 238).—The non-mechanical nature of chemical processes, considered in conjunction with the quantum hypothesis, leads to the conclusion that chemical decomposition is influenced by atomic vibrations. It is assumed that these vibrations are irregular. Formulæ have been deduced for the reaction velocity of different types of chemical processes.

CHEMICAL ABSTRACTS.

**Velocity of Unimolecular Reactions.** ERIC K. RIDGAL (*Phil. Mag.*, 1920, [vi], **40**, 461—465).—A theoretical paper in which unimolecular reactions are considered from the point of view of the radiation hypothesis. It is shown that the reaction velocity of a unimolecular reaction is given by the expression  $dn/dt = \nu \cdot e^{-h\nu/kT}$ , where  $\nu$ , the activating radiation frequency, is identical with the time of molecular relaxation. On the basis of the radiation theory, light would appear to be corpuscular, the size

of a quantum being equal to a wave-length of light. If its energy be due to an electrostatic charge,  $E$ , then  $E^2 = 2hc$ . J. F. S.

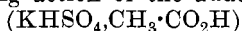
**The Propagation of Flame in Mixtures of Methane and Air. II. Vertical Propagation. III. Propagation in Currents of the Mixtures.** WALTER MASON and RICHARD VERNON WHEELER (T., 1920, 117, 1227—1240).

**Kinetics of the Reaction of Nitrous Acid, particularly towards Halogen Oxyacids.** ALBIN KURTENACKER (*Monatsh.*, 1920, 41, 91—113. Compare A., 1914, ii, 552; 1915, ii, 537, 622).—The action of sodium nitrite in aqueous solution towards potassium chlorate, dichromate, and permanganate in the presence of potassium hydrogen sulphate has been kinetically investigated. With the first two oxidising agents, the solutions of sodium nitrite and potassium hydrogen sulphate are mixed at 20°, and, after a period of about fifteen minutes, during which the solution acquires a steady condition, the agent is added. Aliquot portions of the mixture are removed at definite intervals and almost neutralised by alkali; the nitrous acid is destroyed by protracted ebullition with ammonium sulphate, and the unchanged oxidising agent is estimated by the addition of a measured volume of ferrous sulphate solution, followed by titration of the excess of the latter with  $N/10$ -permanganate solution. In the case of potassium permanganate, reaction proceeds very rapidly, even in dilute solution, and the measurements are effected by noting the time necessary for the decolorisation of a known quantity of permanganate by potassium nitrite in the presence of acetic acid.

The chlorate-nitrite reaction can be expressed by the formula  $dx/dt = [K_1 + K_2 S](\text{ClO}_3')(\text{HNO}_2)$ , where  $K_1$  is the velocity-coefficient of the uncatalysed action,  $K_2$  the acceleration-coefficient of the acid, and  $S$  the concentration of the latter, whilst with dichromate the expression becomes

$$dx/dt = [K_1 + K_2 (S)^2](\text{H}_2\text{Cr}_2\text{O}_7)(\text{HNO}_2).$$

In all probability it is the undissociated nitrous acid, and not the nitrite ion, which takes part in the change. Similarly, the catalytically accelerating action of the added acid



is probably to be attributed to the undissociated molecules (or  $\text{HSO}_4'$  ions), and not to the hydrogen ions. The independence of the rate of reaction of the concentration of the nitrite, which is a feature of the bromate reaction, is not observed in any of the new cases under investigation. Very marked differences are found in the mechanism of the action of chloric, bromic, and iodic acids respectively; the greatest abnormality is observed with bromic acid, which, in contrast with its position in the natural series, acts much more rapidly than either chloric or iodic acid. Further experiments with other oxidising agents will be necessary to elucidate the reasons of this divergent behaviour. Permanganate reacts

much more rapidly with nitrous acid than does any other oxidising agent.

H. W.

**Comparative Rate of Hydrolysis of the Fatty Esters of Different Alcohols.** H. HEINRICH FRANCK (*Seifenfabr.*, 1920, 40, 293—294; from *Chem. Zentr.*, 1920, iii, 337).—In order to investigate the relationship between resorption and rate of hydrolysis of fatty esters, the author has determined the latter factor for linseed oil and for the ethyl and ethylene esters of the fatty acids of this oil. The substances were dissolved in light petroleum and treated with alcoholic-potassium hydroxide solution at 34° or 4°, the free acid being periodically tested. Differences in the rates of hydrolysis were not great, the glyceryl ester being most rapidly, and the ethyl ester least readily, affected. With esters of the polyhydroxy-alcohols, the curves showing the rate of hydrolysis indicate a primary rise followed by a distinct minimum, which is apparently due to temporary formation of the ethyl ester. Enzymic fission by "steapsin Grüber" was also investigated, and the curves again show a minimum after an initial maximum. In agreement with other experiments, the order glyceryl, ethyl, ethylene ester is established.

H. W.

**The Hydrolysis of Platinum Salts. I. Potassium Platinichloride.** EBEN HENRY ARCHIBALD (*T.*, 1920, 117, 1104—1120).

**Significance of Neutral Salts as Catalysts in Chemical Reactions.** OSKAR BAUDISCH (*Biochem. Zeitsch.*, 1920, 106, 134—138).—The author confirms the observation of Wurster (*A.*, 1889, 1242) that hydrogen peroxide and a solution of  $\alpha$ -naphthylamine in dilute acetic acid react, with formation of a colouring matter, in presence of sodium chloride. It is found that this reaction takes place instantaneously in presence of lithium chloride, almost as quickly with magnesium, calcium, or aluminium chloride, and only after the lapse of several minutes with sodium, ammonium, or potassium chloride. The sulphates and nitrates corresponding with these chlorides are inactive in this respect, as also are potassium sodium tartrate and potassium citrate and acetate. In place of  $\alpha$ -naphthylamine, any other readily oxidisable aromatic amine may be employed, but  $\beta$ -naphthylamine does not respond to the reaction. The pronounced effect produced by lithium chloride is doubtless due to the stronger secondary valencies of the lithium in comparison with those of sodium and potassium, the aromatic amine to be oxidised first undergoing loose union with the central lithium atom. The oxidation of aniline salts or of benzidine by means of sodium ammonioprusside in presence of atmospheric oxygen or hydrogen peroxide does not seem to differ fundamentally from the oxidation of aniline acetate by means of hydrogen peroxide in presence of lithium chloride. The well-known oxidation of ammonia to nitrous acid by the agency of

copper hydroxide and atmospheric oxygen is probably of the same character; just as in the oxidation of ammonia by hydrogen peroxide in presence of sodium chloride, the ammonia first enters into co-ordinative union with the central metallic atom, oxidation to nitrous acid by the activated oxygen then occurring readily.

T. H. P.

**Studies in Catalysis. XIV. The Mechanism of the Inversion of Sucrose.** CATHERINE MARGARET JONES and WILLIAM CUDMORE McCULLAGH LEWIS (T., 1920, 117, 1120—1133).

**Catalysis in the Hydrolysis of Esters by Infra-red Radiation.** ERIC KEIGHTLEY RIDEAL and JAMES ARTHUR HAWKINS (T., 1920, 117, 1288—1296).

**Origin of the Elements.** J. H. VINCENT (*Proc. Physical Soc. London*, 1920, 32, 271—290).—A theoretical paper in which hypotheses in connexion with the origin of the elements are put forward. The atomic weights are regarded as the weighted mean values of the atomic weights of the isotopes of the elements, but it is assumed that, as a rule, the atomic weight of the ordinarily occurring element is near to that of some one isotope. Figures and tables are drawn up showing how this accounts for the accepted values of a large number of atomic weights, if it is also assumed that the weights and positions in the periodic table of any isotope are conditioned by laws similar to those holding in the recognised radioactive families. The elements are all supposed to be derived from parent elements by processes known to occur in actively radiating families, but their radioactivity is not, in general, detectable by the usual means, owing to the velocity of expulsion of the particles being low. The possibility of the reversibility of radioactive processes is considered, and regarded as probable in certain cases. Difficulties in connexion with the views expressed are considered. The hypothesis is used to explain the laws (so-called) of the atomic weights of elements of small atomic weight, and the shape of the curve obtained when the atomic weights are plotted against Moseley's numbers.

J. F. S.

**Dimensions of Atoms.** A. O. RANKINE (*Phil. Mag.*, 1920, [vi], 40, 516—519).—A theoretical paper in which the atomic diameter of argon, neon, krypton, xenon, chlorine, bromine, iodine, oxygen, and nitrogen, as found by Bragg from crystal measurements (this vol., ii, 537), are compared with the values found by the author from viscosity measurements (A., 1910, ii, 188, 409, 829; 1912, ii, 332). It is shown that the values obtained by the latter method are somewhat larger than those obtained by the former, but that the increment in the diameter, in passing from one member of a group to the next, is generally about the same in the two sets of values.

J. F. S.

**Constitution and Structure of the Chemical Elements.**

HAWKSWORTH COLLINS (*Chem. News*, 1920, **121**, 157—159).—A continuation of a former paper (this vol., ii, 26), in which elements heavier than manganese are included. The sodium atom is supposed to enter into the constitution of heavier atoms, and the addition of a mass of 23 always corresponds with the gain or loss of one electron. It is shown by calculation that the results cannot be due to chance.

J. R. P.

**Five Main Principles in the Constitution and Structure of the Chemical Elements.**

HAWKSWORTH COLLINS (*Chem. News*, 1920, **121**, 182—185).—(1) Single chemical valencies emanate from elements or portions of elements the masses of which are 1, 3, 7, 23, and 39. (2) The non-metallic nature of an element is always due to a pair or pairs of electropositive forces, each pair emanating from a portion of the element, of which the mass is 4, taking the mass of an atom of hydrogen as unit. (3) Monadic Na (23) takes a prominent part in the formation of all elements of greater mass than itself. (4) In the simpler elements, H (1) forms the connecting link between the other portions, 3, 7, 23, and 39. In the formation of the heavier elements, masses of 23 sometimes unite by forces which are not chemically evident without any intervening unit mass. (5) Each of the heavier elements is formed by the union of simpler elements (which are indicated in each case by mineralogical and chemical facts combined).

J. R. P.

**Representation of the Periodic System of the Elements by a Three-dimensional Spiral.**

GEORG SCHALTENBRAND (*Zeitsch. anorg. Chem.*, 1920, **112**, 221—224).—The elements are arranged in order of atomic weight on an eccentric spiral. The spiral has turns of four kinds of increasing circumference. The first, smallest turn carries the elements hydrogen and helium, and is followed by a larger turn corresponding with the first short period of the periodic table. The short turn is then repeated, carrying neon and fluorine, and in successive similar short turns appear an inactive element and a halogen. The long periods of the table are represented by correspondingly large turns of the spiral, and the largest turn of all carries the rare earth elements. Elements belonging to the same group in the periodic table lie in a vertical plane passing through the axis of the spiral.

E. H. R.

**The Melting Point, Atomic Volume, and the Atomic Number of the Elements, and the Restoring Force of the Atoms.** SUMINOSUKE ONO (*Proc. Phys. Math. Soc. Japan*, 1919, [3], **1**, 251—260).—By means of Lindemann's formula, approximate but simple quantitative relations between the atomic numbers and melting points, etc., are deduced, and are given in the form of charts.

CHEMICAL ABSTRACTS.



**Atomic Forces.** W. KOSSEL (*Zeitsch. Physik*, 1920, 1, 395—415. Compare A., 1916, ii, 243).—A discussion of the general nature of chemical bonding. The two main classes are: (1) heteropolar, where the forces are electrostatic and between different kinds of atoms, depending on the valence electrons, and (2) homopolar, generally between the same kind of atoms or molecules. In (2) the bonding is generally due to the holding of outer electrons in common, and their periodic properties can be predicted by assuming that atoms tend to take up electrons to form the stable 8-configurations of the noble gases. The bonds considered may be those between atoms or between molecules, the two being sometimes indistinguishable, as in the case of the sodium chloride lattice. The two classes may be combined, as in the case of silicon tetrachloride, where the submolecular forces belong to (1) and the intermolecular to (2). The haloids of (1) (alkali and alkaline earth) are characterised by decrease of stability (m. p.) with increasing molecular weight of the halogen, whilst those of (2) show the reverse. Many other periodic characteristics are discussed.

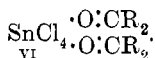
## CHEMICAL ABSTRACTS.

**Percentage Curves of Carbon Compounds.** ALEXANDER JANKE (*Oesterr. Chem. Zeit.*, 1920, 23, 98—101, 106—108).—A mathematical paper in which the numbers of carbon atoms in organic compounds are represented as abscissæ and the percentage of carbon as ordinates. The resulting curve is called a percentage curve. For all hydrocarbons except  $C_nH_{2n}$ , these curves are parabolas. For hydrocarbons,  $C_nH_{2n}$ , they are straight lines. The influence of substitution is considered. J. R. P.

**The Theory of Molecular Compounds.** PAUL PFEIFFER (*Zeitsch. anorg. Chem.*, 1920, 112, 81—96).—In certain respects, Werner's co-ordination formulæ, as applied, for example, to the cobaltammines, are unsatisfactory. It is difficult to understand, for instance, in the hexammine chloride,  $Co[(NH_3)_6]Cl_3$ , how the field of affinity between the cobalt and chlorine atoms can extend over the field of affinity of the ammonia molecules, especially in view of the strong affinity between hydrogen and chlorine. The variation of the total valency of cobalt between 6 and 9 in the cobaltamine group is also difficult to understand. The author applies the principle of "affinity adjustment of the valencies" to overcome the difficulties. In molecular compounds, such as the cobaltammines, the cobalt atom is assumed to have a fixed co-ordinative valence of 6, corresponding with the number of groups in the inner sphere of Werner's formulæ. The ionisable radicles or atoms in the outer sphere are then considered to be combined with the complex radicle as a whole, not attached definitely to the cobalt atom or to any of its associated molecules. The same idea is applied to the complex platinum salts.

Complex organic molecular compounds, such as those formed between aromatic hydrocarbons and di- or tri-nitrobenzene, or between hydrocarbons and quinones, are also considered. There

is, in general, no connexion, for example, between the number of nitro-groups in a compound and the number of aromatic nuclei with which it will combine. In such cases, the compounds are formed by the saturation of polyatomic valence fields on both sides. In some cases it is conceivable that a polyatomic valence field may be saturated by combination with a monatomic field, for instance, when a quinone, with two unsaturated carbonyl oxygen atoms, combines with two benzenoid nuclei. In other classes of compounds, for instance, the compounds between tin tetrachloride and two molecules of a ketone, a compound of the co-ordinative type may be formed, the tin in this case having a co-ordinative valency of 6, thus:



In the crystal structure of simple organic molecular compounds of the type  $AB$ , it is probable that each constituent acts as a co-ordination centre, so that complexes of the type  $AB_6$  and  $BA_6$  interpenetrate, as they do in a rock-salt crystal. This would explain the predominance of the simplest type of such molecular compounds.

E. H. R.

**Back-pressure Valves for Water Filter Pumps.** E. PINOFF (*Chem. Zeit.*, 1920, **44**, 671).—To prevent water passing into a flask under exhaustion from a water-pump, owing to an alteration in the water pressure, a simple valve is inserted by means of rubber tubing between the pump and the flask, manometer, etc. This consists of a short glass tube constricted at each end to a small opening. Within this is a short glass rod, one end of which is fitted into a piece of pressure rubber tubing, whilst the other end is somewhat flattened, and also capped with rubber, a narrow space for the passage of air being left between the rubber tubing and the inner wall of the glass tube. The rod is thus movable, and so long as the pump is working normally is forced against the constriction nearest the pump, still leaving a passage for the air, but should any water enter the tube from the pump, the rod is immediately driven back against the other constriction, the opening in which it seals, so that neither water nor air can enter the flask.

C. A. M.

**Laboratory Apparatus for Delivering Small Quantities of Gas for Admixture with Other Gases in Constant Proportion.** ROBERT MEZGER (*Chem. Zeit.*, 1920, **44**, 658—659).—For the delivery of a constant supply of a gas (for example, ammonia) in definite proportion to another gas, the ammonia is generated by heating ammonium chloride and moistened lime in a round-bottomed flask supported in a basin of mercury. Through the stopper of the flask passes one arm of a T-tube, whilst another branch of this is connected with a mercury thermo-regulator controlling the supply of gas to a Bunsen burner beneath the basin. There is also a pilot flame, with an independent gas supply, adjoin-

ing the Bunsen tube. The other outer limb of the T-piece conducts the ammonia into a capillary tube, which is connected with a wider tube, bending first laterally and then upwards to join a second T-piece. One arm of this communicates with a measured supply of a gas or of air, whilst the other is fitted into a reaction tube packed with glass wool. The pressure is shown on a mercury manometer between the ammonia flask and capillary tube. After removal of air from the apparatus by means of ammonia, the flask is connected with the capillary, and the tap communicating with the thermo-regulator opened. As soon as the pressure rises sufficiently, the gas is cut off from the Bunsen burner, and only the minute flame is left, until the pressure falls again, the gas is re-lighted from the pilot flame, and ammonia again evolved, and so on continuously. The regulation of the ammonia supply is effected by means of the capillary tube. For a definite capillary and kind of gas, the consumption of the gas (in this case ammonia) in c.c. per second ( $v$ ) is found by means of the following modification of Poiseuille's formula,  $v = K \cdot H$ , where  $H$  represents the difference of pressure and  $K$  a constant depending on the capillary and the gas used. In the case of ammonia, it may be found by varying the difference in pressure and estimating each time the corresponding amounts of ammonia by absorption in standard sulphuric acid. By plotting the results for  $v$  in a co-ordinate system, the volume of gas corresponding with any required pressure may be read directly.

C. A. M.

**Lecture Demonstration of the Instantaneous Combination of Bromine with Hydrogen and of the Chlorination of Magnesium in the Form of Magnesium Wool.** OTTO OHMANN (*Ber.*, 1920, **53**, [B], 1429—1430).—Bromine (four to six drops) is placed in a litre gas cylinder, which is shaken until complete evaporation has occurred. The cylinder is brought mouth to mouth with a similar jar filled with hydrogen, and, when diffusion has taken place, the mixture is ignited with a red-hot wire. Combination occurs instantaneously with a perfectly harmless explosion, which is due to the union of excess of hydrogen with residual atmospheric oxygen. If more bromine is used, and in consequence, less air is left, union occurs at once and without explosion, but with production of a peculiar blue flame.

A pad of magnesium wool, lightly sprinkled with finely divided antimony, is fixed to an iron wire and plunged into a jar of chlorine. The spontaneous ignition of the antimony causes the magnesium to burst into vigorous combustion, yielding a product which covers the whole of the inside of the vessel in the form of a snow-white, voluminous powder.

H. W.

**Lecture Experiments. Critical Examination of well-known Experiments with Metallic Sulphides.** R WINDERLICH (*Zeitsch. physikal. Chem. Unterr.*, 1920, **33**, 100—103; from *Chem. Zentr.*, 1920, iii, 429).—Strictly speaking, the union of iron and sulphur cannot be used as an illustration of the

law of constant composition or as an obvious illustration of the differences between mixtures and compounds. A mixture is preferably demonstrated by finely powdered quartz and salt; the mixture of flowers of sulphur and iron filings affords a simple example of a chemical process which, started at one point, proceeds through the whole mass by reason of the great heat of reaction. The statement, common in many elementary text-books, that hydrogen sulphide does not give a precipitate with solutions of ferrous salts is only true when the latter contain mineral acid. The proportions of sulphur and oxide of iron prescribed for demonstration are not in accordance with the amounts calculated from the equation  $2\text{Fe}_2\text{O}_3 + 7\text{S} \rightarrow 4\text{FeS} + 3\text{SO}_2$ , partly because an excess of sulphur must be taken to counterbalance that lost by volatilisation, and partly to inhibit the formation of sulphate, which occurs in the presence of a deficiency of sulphur.

H. W.

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## Inorganic Chemistry.

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**The Preparation of Chlorine from Hydrochloric Acid or Chlorides by means of Nitric Acid.** JULIUS BAUMANN (*Chem. Zeit.*, 1920, **44**, 677).—The chlorine in chlorides or hydrochloric acid can be converted quantitatively into free chlorine by the action of nitric acid of about 52.0% strength, and the whole of the nitric acid recovered unchanged when the proper working conditions are observed. The points to be observed are to charge the chloride, for example, sodium chloride, slowly into the boiling acid and to use a long dephlegmator, whilst a current of air passes into the reacting gases. The following gas reactions involved, namely,  $\text{NOCl} + \text{HNO}_3 = \text{N}_2\text{O}_4 + \text{HCl}$ ,  $2\text{HCl} + \text{N}_2\text{O}_4 = \text{N}_2\text{O}_3 + \text{Cl}_2 + \text{H}_2\text{O}$ , and  $\text{N}_2\text{O}_3 + \text{O}_2 + \text{H}_2\text{O} = 2\text{HNO}_3$ , then have time to complete themselves, and chlorine passes over practically free from hydrochloric acid, whilst the whole of the nitric acid flows back into the reaction vessel.  
E. H. R.

**Electrolytic Formation of Perchlorate from Chlorate.** J. GUILFOYLE WILLIAMS (*Trans. Faraday Soc.*, 1920, **15**, 134—137).—The production of perchlorate by electrolysis is considerably improved if a higher temperature of the liquid is maintained, and the frequent addition of acid improves the efficiency still more. During electrolysis, chloride is produced, and there is an equilibrium value for each temperature.  
J. R. P.

**The Relationship of Iodine and Bromine to Oxygen.** G. GRUBER (*Zeitsch. physikal. Chem. Unterr.*, 1920, **33**, 107—108; from *Chem. Zentr.*, 1920, iii, 434).—Direct replacement of bromine by iodine occurs when the latter acts on an aqueous solution of

potassium bromate; a similar action is not observed with bromine and potassium chlorate. Iodine attacks potassium chlorate in a less simple manner than potassium bromate, the change passing through the phases indicated by the equations  $2\text{KClO}_3 + 2\text{I} + \text{H}_2\text{O} = \text{KHI}_2\text{O}_6 + \text{KCl} + \text{HClO}$ ,  $\text{KHI}_2\text{O}_6 + \text{KCl} + \text{HClO} = 2\text{KIO}_3 + \text{H}_2\text{O} + \text{Cl}_2$ , and  $3\text{HClO} = \text{HClO}_3 + 2\text{HCl}$ . H. W.

**Preparation of Thionyl Fluoride and Attempts to Prepare Carbonyl Fluoride.** WILHELM STEINKOPF and JULIUS HEROLD (*J. pr. Chem.*, 1920, [ii], 101, 79—81).—A modified method of preparing thionyl fluoride by the interaction of thionyl chloride and arsenic fluoride is described. A brass flask is provided with an upright condenser, which is connected by a bent tube to a second condenser cooled with ice-water, which leads to a leaden vessel cooled to  $-50^\circ$  to  $-60^\circ$ . The flask is initially cooled by ice and contains the arsenic fluoride, to which the calculated quantity of thionyl chloride is gradually added through a dropping funnel; the latter is then removed, and the flask is slowly warmed to about  $80^\circ$ , when the thionyl fluoride distils into the leaden receiver, whilst arsenic fluoride and chloride and thionyl chloride are held back by the reflux condenser. The attempts to prepare carbonyl fluoride were not completely successful, probably because platinum apparatus was not available. The best results were obtained by heating a mixture of arsenic fluoride and carbonyl chloride in a lead-lined iron or brass vessel provided with an upright condenser; the process is carried out during several hours on the water-bath with intermittent condensation of the products. Impure carbonyl fluoride was thus obtained as a readily decomposable substance, which solidified in liquid air and had b. p. about  $-160^\circ$  to  $-150^\circ$ . H. W.

**The Decomposition of Persulphuric Acid.** HERMAN PALME (*Zeitsch. anorg. Chem.*, 1920, 112, 97—130).—The rate of decomposition of potassium persulphate in solutions of 5.0, 7.53, and 10*N*-sulphuric acid at  $50^\circ$  has been studied. Since the reaction proceeds through the stages, persulphuric acid  $\rightarrow$  Caro's acid  $\rightarrow$  hydrogen peroxide, it was necessary to develop a method for estimating these substances when all present in the same solution. Advantage was taken of the fact that Caro's acid reacts immediately with potassium iodide, whilst hydrogen peroxide reacts much more slowly, and persulphuric acid slowest of all. A sample of the solution is mixed with potassium iodide and titrated rapidly with sodium thiosulphate, the time taken being noted, so that a correction can be applied for the small quantity of iodine liberated by the hydrogen peroxide and persulphuric acid. The quantity of Caro's acid is thus found. A second sample is then treated with potassium iodide and titrated with sodium sulphite, which reduces hydrogen peroxide. This second titration gives the sum of Caro's acid and hydrogen peroxide. Finally, the persulphuric acid is estimated in a third sample by adding the calculated quantity of

sodium sulphite to reduce the other two compounds, and estimating the persulphuric acid by the ferrous sulphate-permanganate method. The dilution for the titrations corresponded with 2.0 grams of potassium persulphate per litre, of which 200 c.c. were titrated at a time.

The experiments showed that, within the limits of error, the two reactions,  $\text{H}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} \xrightleftharpoons{k_1} \text{H}_2\text{SO}_5 + \text{H}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_5 + \text{H}_2\text{O} \xrightleftharpoons{k_2} \text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4$ , can be regarded as unimolecular and irreversible. With increasing concentration of sulphuric acid, both velocity-constants increased at a greater rate than the acid concentration, but the ratio  $k_1/k_2$  remained constant, 39.8. No relation between hydrogen-ion concentration and velocity of reaction could be discovered, and the conclusion of Levi and Migliorini (A., 1907, ii, 81) that undissociated persulphuric acid, the presence of which would be favoured by increasing hydrogen-ion concentration, is less stable than its salts, was not confirmed. The experiments were not carried far beyond the time after which oxygen begins to be evolved, through the reaction  $\text{H}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O}_2 = 2\text{H}_2\text{SO}_4 + \text{O}_2$ , but it was shown that the velocity of this reaction increases considerably with decreasing concentration of acid. Friend's results (T., 1906, 89, 1092), which showed that the reaction is unimolecular, can be explained on the assumption that Caro's acid is first formed from persulphuric acid, and then reacts with hydrogen peroxide. Persulphuric acid probably does not itself react with hydrogen peroxide.

E. H. R.

### Determination of the Rate of Solution of Atmospheric Nitrogen and Oxygen by Water. III. W. E. ADENEY and H. G. BECKER (*Sci. Proc. Roy. Dublin Soc.*, 1920, 16 [N.S.], 143—152).—A continuation of experiments previously reported (see A., 1919, ii, 104, 510). The rate of solution of air in quiescent water under laboratory conditions was determined. The results show that the process of solution under these conditions consists in solution at the surface with slow mixing in the body of the liquid. The results are represented by a formula, $dw/dt = a - bw$ , where $w$ = total quantity of gas in solution at any moment, $t$ = time, and $a$ and $b$ are constants depending on the size of the apparatus. The water was contained in vertical tubes exposed to air. The rate of solution depends on the humidity of the air, being greater with dry than with moist air.

J. R. P.

### Very High Pressures and the Synthesis of Ammonia.

GEORGES CLAUDE (*Bull. Soc. chim.*, 1920, [iv], 27, 705—724).—A lecture delivered before the French Chemical Society and the Society for the Encouragement of National Industry. W. G.

**Fractionation of Nitric Acid.** JULIUS BAUMANN (*Chem. Zeit.*, 1920, 44, 678).—Experiments on the fractionation of nitric acid were made, using a litre flask fitted with a dephlegmator 200 cm. long, inclined at 45°, with a jacket for heating it to any desired temperature. A mixture of 250 c.c. of water and 250 c.c. of

nitric acid (D 1.4; 69.8%, the constant boiling mixture) was distilled with the dephlegmator heated at  $100^{\circ}$ , and there were obtained 250 c.c. of distillate, containing only 0.02%  $\text{HNO}_3$ , and 250 c.c. of residual nitric acid, 69.5% in strength. Practically complete separation was therefore obtained. In another experiment, 500 c.c. of 91.5%  $\text{HNO}_3$  were distilled with the dephlegmator heated at  $86^{\circ}$ , the boiling point of pure nitric acid. There were obtained in the distillation flask 140 c.c. of 70.1%  $\text{HNO}_3$ , and in the receiver 350 c.c. of 100.5%  $\text{HNO}_3$ . Thus a practically complete separation into pure nitric acid and the constant boiling mixture, b. p.  $123^{\circ}$ , was obtained. E. H. R.

**Reduction of Nitrites and Nitrates.** OSCAR BAUDISCH and PAUL MAYER (*Biochem. Zeitsch.*, 1920, **107**, 1—42).—Nitrites are reduced quantitatively by excess of ferrous hydroxide in neutral and alkaline solution. In boiling solutions made alkaline with carbonates, nitrous oxide and ammonia are chiefly formed. In boiling alkali hydroxide solution, the nitrite is quantitatively reduced to ammonia. Alkali nitrates are reduced quantitatively by ferrous hydroxide in neutral solution and in alkaline solution containing 28% of sodium hydroxide. Starting with neutrality, the amount of nitrate reduced diminishes until the alkali content is 6.5% of sodium hydroxide, when a minimum is reached; beyond that limit, the amount reduced increases with the increase of alkali until the maximum is reached at the concentration of 28% of sodium hydroxide. Up to a concentration of 6.5% of sodium hydroxide, oxygen is necessary for the reduction. With higher alkali concentrations, reduction also takes place in the absence of oxygen. At an alkali concentration of 6.5% of sodium hydroxide, the amount of nitrate reduced is proportional to the amount of nitrate present in solution, and is in a condition of adsorption by the ferrous hydroxide. The above observations are utilised for the estimation of nitrites and nitrates separately and when together. S. S. Z.

**Equilibrium of the Four-component System:  $\text{Na}_2\text{SO}_4$ ,  $\text{NaHCO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{HCO}_3$ , and  $\text{H}_2\text{O}$ .** KYOSUKE NISHIZAWA (*J. Chem. Ind. Tokyo*, 1920, **23**, 25—43).—To study the best condition for the manufacture of ammonium sulphate by the ammonia-soda process from sodium sulphate, detailed studies were made of the equilibrium of a system consisting of these four components. first 2-component, then 3-component, and finally 4-component systems being determined. Ammonium hydrogen carbonate was prepared for each experiment. The concentration of the sodium sulphate and the ammonium sulphate was determined by the barium chloride and the Kjeldahl methods, respectively, and that of both bicarbonates by titration, using methyl-orange as indicator. The results are tabulated in sixteen tables and two curves. The results obtained from invariant systems are as follows:



Solid Phases.	Composition of the solution in gram-mol. to 1000 gram-mol. H <sub>2</sub> O.			
	Na <sub>2</sub> SO <sub>4</sub> .	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .	NH <sub>4</sub> HCO <sub>3</sub> .	NaHCO <sub>3</sub> .
Na <sub>2</sub> SO <sub>4</sub> .10H <sub>2</sub> O .....	16.61	—	—	—
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .....	—	10.05	—	—
NH <sub>4</sub> HCO <sub>3</sub> .....	—	—	42.52	—
NaHCO <sub>3</sub> .....	—	—	—	18.53
Na <sub>2</sub> SO <sub>4</sub> .10H <sub>2</sub> O ; NaHCO <sub>3</sub> .	14.18	—	—	12.75
Na <sub>2</sub> SO <sub>4</sub> .10H <sub>2</sub> O ; Na <sub>2</sub> SO <sub>4</sub> .(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .4H <sub>2</sub> O	31.54	45.14	—	—
Na <sub>2</sub> SO <sub>4</sub> .(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .4H <sub>2</sub> O ; (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .....	13.74	94.86	—	—
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ; NH <sub>4</sub> HCO <sub>3</sub> ....	—	96.40	14.91	—
NaHCO <sub>3</sub> ; NH <sub>4</sub> HCO <sub>3</sub> .....	—	—	38.92	12.79
Na <sub>2</sub> SO <sub>4</sub> .10H <sub>2</sub> O ; NaHCO <sub>3</sub> ; Na <sub>2</sub> SO <sub>4</sub> .(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .4H <sub>2</sub> O	26.22	45.86	—	12.84
NaHCO <sub>3</sub> ; NH <sub>4</sub> HCO <sub>3</sub> ; Na <sub>2</sub> SO <sub>4</sub> .(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .4H <sub>2</sub> O	12.46	67.08	—	20.90
NH <sub>4</sub> HCO <sub>3</sub> ; (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ; Na <sub>2</sub> SO <sub>4</sub> .(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .4H <sub>2</sub> O	6.79	97.99	—	14.96

## CHEMICAL ABSTRACTS.

**Cæsium Bromate.** C. R. McCrosky and Harold D. Buell (*J. Amer. Chem. Soc.*, 1920, **42**, 1786—1789).—The preparation of cæsium bromate is probably best carried out in acid solution. Cæsium bromate is a definite crystalline salt without water of crystallisation. Occluded water causes decrepitation. Its melting point (not yet determined) is above that of potassium bromate. After fusion, the salt soon decomposes, evolving a large amount of oxygen and leaving a bromide. The solubility of the salt is 4.53 grams in 100 grams of water at 30°. J. R. P.

**A New Rubidium (Cæsium)–Silver–Gold Compound and its Application to the Microchemical Detection of Gold, Silver, Rubidium, and Cæsium.** ERICH BAYER (*Monatsh.*, 1920, **41**, 223—241. Compare Emich, A., 1919, ii, 171).—Characteristic crystalline precipitates are formed when solutions of rubidium or cæsium chloride are mixed with gold and silver solutions; rubidium–silver–gold chloride forms blood-red prisms and platelets, whilst the cæsium compound crystallises in opaque cubes and stars. The composition of the compounds corresponds with the formulæ Ag<sub>x</sub>Au<sub>2-x/3</sub>Cl<sub>6</sub>.3RbCl and Ag<sub>x</sub>Au<sub>2-x/3</sub>Cl<sub>6</sub>.3CsCl (where 0 ≤ x ≤ 6), in which gold and silver are mutually replaceable components. For rubidium, silver, and gold, the atomic proportions observed are in the ratio 3:0.81—1.04:1.5—1.4, whilst for the cæsium compound the corresponding ratio is 3:0.4—1.18:1.82—1.64. The limiting compounds, Ag<sub>2</sub>CsCl<sub>3</sub> and Au<sub>2</sub>Cs<sub>3</sub>Cl<sub>9</sub>, do not appear to have been prepared, but Marsh and Rhymes (*T.*, 1913, **103**, 782) have examined the analogous substances, Ag<sub>2</sub>CsI<sub>3</sub> and Ag<sub>2</sub>RbI<sub>3</sub>.

The crystals are adapted to the microchemical identification of gold, silver, rubidium, and cæsium, the smallest quantities recognisable in this manner being 0.1, 0.01, 0.1, and 0.1 microgram respectively. H. W.

**A New Rubidium (Cæsium)-Silver-Gold Compound and its Application to the Microchemical Detection of Gold, Silver, Rubidium and Cæsium.** FRIEDRICH EMICH (*Monatsh.*, 1920, **41**, 243—252. Compare Bayer, preceding abstract; Emich, A., 1919, ii, 171).—A theoretical paper in which ideas are developed based on Bayer's observation that univalent silver and tervalent gold are mutually replaceable in the rubidium (cæsium)-silver-gold chlorides.

It is suggested that elements in general have a far greater power of mutual replaceability than has previously been assumed, and that this is frequently the cause of the great difficulty experienced in isolating absolutely pure substances. Elements in general may be classified as (1) isotopic elements, the separation of which is impossible by precipitation or crystallisation; (2) isomorphous elements, which can only be incompletely separated; and (3) readily separable elements. The most general conception of the union of two substances is obtained by regarding it as controlled by the two factors, affinity in the narrower sense, due to the attraction of the atoms or molecules caused by harmonic vibration, and cohesive forces in the sense of the entropy rule. Both influences are, in general, operative, but the first predominates in chemical compounds, the second in isomorphous and isotopic mixtures. Between the limiting cases, which are generally well defined, because the controlling factors are usually of a widely differing order of magnitude, there are a number of transition examples, such as the rubidium-gold-silver compounds. It should be noted that this hypothesis involves the consideration of the laws of constant and multiple proportions, like the gas laws, as only approximately accurate.

Bayer's compounds are discussed at length, and it is pointed out that the limiting compounds,  $\text{RbCl}_2\text{AgCl}$  and  $3\text{RbCl}_2\text{AuCl}_3$ , are not known, and that the stability of the molecule is increased by the entrance of a third component, and that the heavier cæsium has a more marked effect than the lighter rubidium. Re-examination of the triple nitrites has proved that there is a greater tendency towards mutual replacement among the bivalent than among the univalent elements, but the phenomena are not so well defined as with Bayer's salts.

Contrary to the previous observation (Emich, *loc. cit.*), it is now found that the place of rubidium cannot be taken by potassium in the triple chloride, and the value of the method for the microchemical detection of cæsium and rubidium is thereby greatly enhanced.

H. W.

**Ammonium Silicate. IV. The Ageing and Transformation of Silicic Acid Gel and the Course of the Solution of Silicic Acid in Ammonia.** ROBERT SCHWARZ and OTTO LIEDE (*Ber.*, 1920, **53**, [B], 1509—1518. Compare this vol., ii, 175; A., 1917, ii, 31; 1919, ii, 283).—The authors have examined the behaviour of silica gel when slowly dried at the ordinary temperature and are led to the conclusion that the age

ing process consists in the condensation of  $(\text{SiO}_2)_x$  to  $(\text{SiO}_2)_{2x}$ , and that this occurs without any change in the appearance of the gel; further changes in the system  $\text{SiO}_2\text{--H}_2\text{O}$  then occur, leading to the formation of  $(\text{SiO}_2)_{3x}$ , which is indicated by the incipient formation of cloudy particles in the colourless, transparent mass. Precisely similar phenomena are observed when the gel is dehydrated by being heated, but, for some unexplained reasons, a much greater loss of water appears to be necessary in this case before the end-point is reached.

The solubility of silicic acid in ammonia has been examined in a modified manner, since it has been found that the older measurements, in which glass vessels were used, are very greatly influenced by the alkali from the glass. The hydrated silica and ammonia are mixed in the quartz vessel which serves for the measurement of the electrical conductivity. After definite intervals, portions of the solution are filtered through paper, which retains suspended silica, and the filtrates are passed through an ultra-filter to retain colloidal particles. The silica retained by the paper and that in the final filtrate are estimated. It is found that equilibrium is attained after about seventy-two hours at  $18^\circ$ , and that the solution contains 64% of the silica in true solution, 8% in colloidal solution, and 28% undissolved. The conductivity and solubility curves show that the amount of dissolved silica increases during the whole course of the experiment, whilst the colloidal silica gradually diminishes in quantity. The former therefore grows at the expense of the latter, and it appears justifiable to conclude that the formation of the colloidal solution is the primary process which is followed by the production of the molecular solution.

H. W.

**Solubility of Calcium Carbonate.** YUKICHI OSAKA (*J. Tokyo Chem. Soc.*, 1920, **41**, 453—468).—On the assumption that only a small part of the carbon dioxide dissolved in water is combined with the water, and that consequently carbonic acid is a much stronger acid than acetic acid, the author has recalculated the solubility product of calcium carbonate from the data of McCoy and Smith on the solubility of calcium carbonate under different carbon dioxide pressures, using  $K=3.50 \times 10^{-7}$ ,  $K_2=4.91 \times 10^{-11}$ , and has obtained the value  $7.24 \times 10^{-9}$ . The number of gram-molecules of calcium carbonate dissolved by 1 litre of water ( $C$ ) under any known carbon dioxide pressure ( $P$ ) is given by the formula

$$C = [\text{Ca}^{++}] + (1 - y)/2\gamma[\text{HCO}_3'],$$

where  $\text{Ca}^{++} = (5.24 \times 10^{-17} + 2.49 \times 10^{-12}P^{\frac{1}{2}} + 2.97 \times 10^{-8}P^{\frac{1}{4}})/(2.91 \times 10^{-6}P)$  and  $\text{HCO}_3' = (2.61 \times 10^{-6}P)/(7.24 \times 10^{-9} + 1.72 \times 10^{-4}P^{\frac{1}{2}})$ , and  $y$  = the degree of dissociation of calcium acetate having the same concentration of acetate ion as the bicarbonate ion.

CHEMICAL ABSTRACTS.

**Monoclinic Double Selenates of the Copper Group.** A. E. H. TUTTON (*Proc. Roy. Soc.*, 1920, [A], **98**, 67—95).—The

four double selenates of the series  $R_2M(SeO_4)_2 \cdot 6H_2O$ , in which M is copper and R is potassium, rubidium, caesium, or ammonium, have been examined crystallographically. They form a group in the extensive series of isomorphous monoclinic double sulphates and selenates which have been examined by the author, and the four salts exhibit the same relationships one to another as in similar groups of potassium, rubidium, caesium, and ammonium salts. As was found in the case of the double sulphates, so in the double selenates, the constants, both physical and morphological, of the salts of the copper group differ considerably in their absolute values from those of the magnesium, zinc, iron, nickel, and cobalt groups (A., 1919, ii, 346).

The salts all crystallise in the holohedral-prismatic class of the monoclinic system. Potassium copper selenate,  $K_2Cu(SeO_4)_2 \cdot 6H_2O$ ,  $a:b:c=0.7508:1.05143$ ,  $\beta=103^\circ 25'$ ,  $D_4^{20} 2.539$ . Rubidium copper selenate,  $Rb_2Cu(SeO_4)_2 \cdot 6H_2O$ ,  $a:b:c=0.7495:1.05066$ ,  $\beta=104^\circ 44'$ ,  $D_4^{20} 2.839$ . Caesium copper selenate,

$Cs_2Cu(SeO_4)_2 \cdot 6H_2O$ ,  
 $a:b:c=0.7398:1.04981$ ,  $\beta=105^\circ 42'$ ,  $D_4^{20} 3.073$ . Ammonium copper selenate,  $(NH_4)_2Cu(SeO_4)_2 \cdot 6H_2O$ ,  $a:b:c=0.7476:1.05150$ ,  $\beta=105^\circ 30'$ ,  $D_4^{20} 2.223$ .

The optical constants of the crystals were determined, and for each salt the axial ratios of the optical indicatrix and the molecular refraction and dispersion were calculated. E. H. R.

**Comparative Study of the Decomposition of a Dissociable Mercurous Chloride obtained from Mercuric Chloride and of the Ordinary Form.** GAMBIER (*Ann. malad. vénér.*, 15, 28—31; from *Chem. Zentr.*, 1920, iii, 331).—Duret's observations (A., 1919, ii, 232) are confirmed, and, by variation of the precipitating and reducing agent, it has been found possible to secure a more voluminous and still more readily dissociable preparation which is quite free from mercuric chloride. The separation of free mercury has been estimated colorimetrically. The preparation gives 2.0 times at  $15^\circ$ , 2.4 times at  $30^\circ$ , 2.66 times at  $60^\circ$ , and 1.5 times at  $100^\circ$  as much mercury as does ordinary calomel, and the equilibrium between eliminated mercury and the unchanged molecule is very rapidly attained. H. W.

**Inflammation of a Mixture of Aluminium and Sodium Peroxide by means of Water.** OTTO OHMANN (*Ber.*, 1920, 53, [B], 1427—1429).—An intimate mixture of finely divided aluminium (1 gram) and sodium peroxide (4.3 grams) is readily inflamed with slight explosion by the addition of a few drops of water. The experiment is best adapted to lecture purposes by sprinkling a small quantity of the powder on the surface of water, when it forms a thin skin without becoming inflamed; subsequent addition of more powder is then accompanied by inflammation. The suitability of the specimen of sodium peroxide should be ascertained, as its quality is liable to considerable variation.

H. W.

**The Oxidising Properties of Sulphur Dioxide. I. Iron Chlorides.** WILLIAM WARDLAW, and FRANCIS HERBERT CLEWS (T., 1920, 117, 1093—1103).

**The Oxidising Properties of Sulphur Dioxide. II. Iron Phosphates.** WILLIAM WARDLAW, SIDNEY RAYMOND CARTER, and FRANCIS HERBERT CLEWS (T., 1920, 117, 1241—1247).

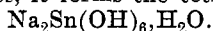
**Oxydase-like Action of Some Complex Salts of Metals.** YUJI SHIBATA and KEITA SHIBATA (*J. Tokyo Chem. Soc.*, 1920, 41, 35—53. Compare Colin and Liévin, A., 1919, i, 430).—Using a 0·001*M*-alcoholic solution of myricetin to indicate the oxydase-like action, the authors have examined about fifty complex salts of cobalt, nickel, copper, zinc, cadmium, chromium, and iron, and find that the most reactive salts are those containing strong acid radicles or metals which give unstable complex ions in aqueous solution; for example, 1:6-dichlorotetrammincobalt chloride (in 0·001*M*-solution) produces a bright red or purple coloration instantly, pentamminecupric sulphate less markedly, dichloroethylenediaminechromium chloride very feebly, and potassium ferro- or ferricyanide not at all.

The four factors which operate against the oxydase-like action are (1) hydrogen ions, (2) inactive complex salts, (3) hydroxylamine, mercuric chloride, and a few other substances, (4) heating at 80—90°. Valency plays no part, the reaction depending wholly on the instability of the salts in water.

The application of these active complex salts to lacquers hastens drying to a marked degree.

CHEMICAL ABSTRACTS.

**Salts of Stannic and Plumbic Acids.** HANS ZOCHER (*Zeitsch. anorg. Chem.*, 1920, 112, 1—66).—A study of stannates and plumbates was undertaken with the object of elucidating the so-called semi-colloidal state, with a critical discussion of which the paper opens. The methods for preparing and analysing alkali stannates are described. Sodium stannate crystallises from sodium hydroxide solutions at ordinary temperatures as the trihydrate,  $\text{Na}_2\text{Sn}(\text{OH})_6$ ; it is practically insoluble in 7·0*N*-sodium hydroxide. When precipitated by sodium hydroxide at 0° or by alcohol at 0°, or ordinary temperatures, it forms the tetrahydrate,



The solubilities of the two hydrates were determined between -5° and 50°; that of the trihydrate, the less soluble salt, which may be regarded as an "anhydride," diminishes with increasing temperature, whilst that of the tetrahydrate increases. The transition point was difficult to determine by the dilatometric method, but from the solubility curves appears to be close to -5°. The trihydrate forms a eutectic with water at -11°, the tetrahydrate at -7°. In addition, a third hydrate, approximating to  $\text{Na}_2\text{Sn}(\text{OH})_6 \cdot 18\text{H}_2\text{O}$ , was discovered, which has a transition point to the "anhydride" at 1°. The hydrolysis of sodium stannate in aqueous solutions was

studied by means of potential measurements. In normal solutions the hydrolysis is about 2.7%, and appears to be complete at a dilution of  $1/3000N$ . In normal solutions of the stannate the extent of hydrolysis gradually increases with time. This phenomenon is discussed in connexion with similar observations in the case of other colloidal solutions and of solutions of tin tetrachloride. There is no evidence of adsorption of alkali by sodium stannate under any conditions.

Lithium stannate forms an "anhydride,"  $\text{Li}_2\text{Sn}(\text{OH})_6$ , isomorphous with the sodium salt, and also a dihydrate of this salt,  $\text{Li}_2\text{Sn}(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ . The solubilities of both salts were determined between  $28^\circ$  and  $80^\circ$ . The two curves are approximately parallel, the solubilities increasing with the temperature; the transition point could not be found, but is probably below  $100^\circ$ . Potassium stannate forms an "anhydride,"  $\text{K}_2\text{Sn}(\text{OH})_6$ , and also a mono- and dihydrate of this salt. The solubilities are greater than those of the sodium and lithium salts.

In the course of a long discussion on the chemistry of stannic oxide from the colloidal point of view, the following points are elucidated. The low crystallisation velocity of the oxide, resulting from its slight solubility, facilitates its assumption of the colloidal state. The "ageing" of the colloid is accelerated or retarded by various influences, particularly by accompanying salts in solution. Coagulation, that is, the coalescence of the bounding surfaces of the colloidal particles in solution, is retarded by the electrostatic charge on the particles.

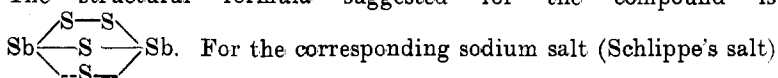
The work was also extended to the plumbates. Sodium plumbate was prepared by dissolving freshly precipitated lead peroxide, in small quantities at a time, in boiling concentrated (8—10*N*) sodium hydroxide solution. The salt is very sparingly soluble in this solution, and separates in crystals which appear to be isomorphous with sodium stannate. Although the analyses of the crystals always showed excess of  $\text{Na}_2\text{O}$ , their composition is taken to be  $\text{Na}_2\text{Pb}(\text{OH})_6$ . Lithium plumbate was also prepared, and appeared, from its crystalline form, to be isomorphous with the sodium salt. The properties of plumbic acid are discussed from the colloidal point of view.

E. H. R.

**Antimony Pentasulphide (Sulphur auratum).** F. KIRCHHOFF (*Zeitsch. anorg. Chem.*, 1920, **112**, 67—80).—The ordinary golden antimony sulphide is described in the literature as consisting of a mixture of pentasulphide and trisulphide, with more or less free sulphur. The purest form of the substance contains about 8% of sulphur, which can be extracted with carbon disulphide or acetone, the residue having a composition corresponding with the formula  $\text{Sb}_2\text{S}_4$ . This form is obtained by the action of dilute acids on Schlippe's salt, according to the equation  $2\text{Na}_3\text{SbS}_4 + 6\text{HCl} \rightarrow \text{Sb}_2\text{S}_4 + \text{S} + 6\text{NaCl} + 3\text{H}_2\text{S}$ . It is shown in the present paper that antimony pentasulphide has no existence, but that golden antimony sulphide is a mixture of  $\text{Sb}_2\text{S}_4$  with from 0 to 50%  $\text{Sb}_2\text{S}_3$  and a vary-

ing amount of free sulphur, according to the method of preparation. The compound  $\text{Sb}_2\text{S}_4$  has been prepared in a pure state from zinc thioantimonate. The latter salt,  $\text{Zn}_3\text{Sb}_2\text{S}_8$ , was prepared by the interaction of Schlippe's salt and zinc chloride. It formed a chrome-yellow precipitate, which when dried and ground had a bright orange-red colour. The crude substance contained about 6.7% of extractable sulphur, and after removal of this, its composition corresponded exactly with the above formula. The zinc thioantimonate is decomposed by dilute acids according to the equation  $\text{Zn}_3\text{Sb}_2\text{S}_8 + 6\text{HCl} \rightarrow \text{Sb}_2\text{S}_4 + 3\text{ZnCl}_2 + \text{H}_2\text{S}_2 + 2\text{H}_2\text{S}$ . Analysis of the orange-red residue from this reaction showed it to have the composition  $\text{Sb}_2\text{S}_4$ , the same as that of the pure extracted orange form of golden antimony sulphide.

The sulphide  $\text{Sb}_2\text{S}_4$  is to be regarded as a special case of compounds of the type  $\text{M}_x(\text{SbS}_4)_y$ , in which M becomes Sb and  $x=y$ . The structural formula suggested for the compound is



the structure becomes  $\begin{array}{c} \text{Na} \text{---} \text{S} \text{---} \text{S} \\ \text{Na} \text{---} \text{S} \text{---} \\ \text{Na} \text{---} \text{S} \text{---} \end{array} \text{Sb}$ , and a corresponding formula

is suggested for the zinc salt. The colour of the compound  $\text{Sb}_2\text{S}_4$  and of the thioantimonates of the heavy metals is attributed to the presence of closed ring systems in the structure of these compounds. The sodium salt, in which there is no closed ring, is colourless. The

red antimony trisulphide probably has the structure  $\text{Sb} \begin{array}{c} \diagup \text{S} \diagdown \\ \text{---} \text{S} \text{---} \\ \diagdown \text{S} \diagup \end{array} \text{Sb}$ .

E. H. R.

**Revision of the Atomic Weight of Bismuth. Analysis of Bismuth Chloride.** O. HÖNIGSCHMID and L. BIRCKENBACH (*Zeitsch. Elektrochem.*, 1920, **26**, 403—408).—See this vol., ii, 549.

**The Binary System Lead-Bismuth.** W. HEROLD (*Zeitsch. anorg. Chem.*, 1920, **112**, 131—154).—The limits of the eutectic range in the lead-bismuth alloys have been determined by different observers, generally by thermal methods, with divergent results. These limits have now been investigated by studying the electrical conductivity and hardness of the alloys and their microscopic structure. Special precautions were taken to obtain uniform specimens by careful annealing. The conductivity experiments, which were made at 123° and 0°, indicated for the limit of solubility of bismuth in lead, 17.5 to 18.5% Bi, and for the solubility of lead in bismuth, 1.6% Pb. The interpretation of the results of the hardness experiments was uncertain owing to the influence of the treatment which any particular sample had undergone on its hardness. The hardness-composition curve had a wave-form with an inflexion corresponding approximately with the eutectic point. The hard

ness of the eutectic does not appear to derive additively from that of the two series of mixed crystals. The curve indicates the mixed crystal limit on the lead side at about 17–18% Bi. The microscopic experiments showed that a sample containing 40% Bi contained no trace of eutectic after annealing eight hours at 124°. Alloys with more than 40% Bi showed eutectic after thirty hours at 40°. It is concluded that the two limits for the eutectic are 40% Bi and 0.2–0.5% Pb.

E. H. R.

### Normal Bismuth Tungstate and Molybdate: their Relations to the Corresponding Lead Compounds.

F. ZAMBONINI (*Gazzetta*, 1920, 50, ii, 128–146).—The author has prepared and examined, especially crystallographically, normal bismuth tungstate and molybdate, and has subjected the two systems,  $\text{PbWO}_4\text{--Bi}_2(\text{WO}_4)_3$  and  $\text{PbMoO}_4\text{--Bi}_2(\text{MoO}_4)_3$ , to thermal analysis.

Normal bismuth tungstate,  $\text{Bi}_2(\text{WO}_4)_3$ , is dimorphous, and crystallises in (1) the monoclinic system,  $a:b:c=1.006:1.1520$ ,  $\beta=90^\circ 34'$ ,  $D^{25}_4 8.24$ , and (2) the tetragonal system,  $a:c=1.1566$ . The latter phase corresponds perfectly with the tetragonal phase both of the normal molybdates and tungstates of the elements of the yttrium and cerium group, as well as of those of the isomorphogenic elements of the calcium–strontium–barium–lead group, the value of  $a:c$  in these compounds varying from 1.1542 to 1.1623. The monoclinic form is distinctly pseudo-tetragonal, the axial ratios differing but little from 1.1:1.566 and the value of  $\beta$  but little from  $90^\circ$ . This monoclinic form exhibits undeniable crystallographic resemblances to raspite, the monoclinic form of lead tungstate, but the tetragonal bismuth tungstate shows far closer resemblances to stolzite, the tetragonal form of lead tungstate.

Normal bismuth molybdate,  $\text{Bi}_2(\text{MoO}_4)_3$ , was obtained only in the tetragonal form,  $a:c=1.15636$ ,  $D^{25}_{15} 6.07$ , the crystallographic constants and the molecular volume differing little from those of the molybdates of the cerium metals and of lead.

Monoclinic bismuth tungstate has m. p.  $832^\circ$ , tetragonal bismuth molybdate, m. p.  $643^\circ$ , and lead tungstate and molybdate, m. p.  $1130^\circ$  and  $1065^\circ$  respectively. For the system  $\text{Bi}_2(\text{WO}_4)_3\text{--PbWO}_4$  the melting-point diagram has the form characteristic for binary mixtures, either forming no solid solutions or exhibiting extremely limited mutual solubility in the solid state. The crystallisation curve first falls rapidly from  $1130^\circ$  to a eutectic point at about  $813^\circ$  corresponding with about 73 mol. % of  $\text{Bi}_2(\text{WO}_4)_3$ , and then rises directly to  $832^\circ$ . The system  $\text{PbMoO}_4\text{--Bi}_2(\text{MoO}_4)_3$  shows quite similar behaviour, the crystallisation curve descending rapidly from  $1065^\circ$  to a eutectic at about  $615^\circ$ , corresponding with about 71.5 mol. % of  $\text{Bi}_2(\text{MoO}_4)_3$ , and then rises directly to  $643^\circ$ . With both systems the form of the curve of eutectic arrests indicates that the eutectic disappears completely only in the pure components.

T. H. P.



## Mineralogical Chemistry.

**Zinc-blende in the Basalt of Bühl, near Cassel.** W. EITEL (*Centr. Min.*, 1920, 273—285).—Black zinc-blende intimately associated with quartz, and sometimes pyrrhotite or pyrites, occurs as enclosures in the basalt. Analyses show it to be of the marmatite variety with  $\text{FeS}:\text{ZnS}=1:4$  and  $1:3$  in the two analyses respectively:

	Fe.	Mn.	Zn.	Cd.	S.	Gangue.	Total.	Sp. gr.
I.	12.28	trace	52.02	—	32.08	3.52	99.90	—
II.	19.50	trace	48.08	trace	31.79	0.98	100.35	4.033

The presence of the mineral is attributed to the basalt breaking through a mineral-vein and enveloping fragments of the same. It is supposed that the original pyrites was largely dissociated to ferrous sulphide, which was partly absorbed by the zinc sulphide, the remainder being represented by the pyrrhotite. L. J. S.

**Ultrabasite, a New Mineral from Freiberg, Saxony.** V. ROSICKÝ and J. ŠTĚRBA-BÖHM (*Zeitsch. Kryst. Min.*, 1920, 55, 430—439; *Rozpr. České Akad.*, 1916, 25, No. 45).—The black crystals with metallic lustre and black streak are orthorhombic ( $a:b:c=0.988:1:1.462$ ) with a tetragonal habit.  $H\ 5$ ,  $D\ 6.026$ . They are associated with quartz, rhodochrosite, galena, and proustite on gneiss. Analysis gave:

Sb.	Ag.	Pb.	Cu.	Fe.	Ge.	S.	Total.
4.60	22.35	54.16	0.47	0.25	2.20	16.15	100.18

agreeing with the ultrabasic formula  $\text{Sb}_4\text{Ag}_{22}\text{Pb}_{28}\text{Ge}_3\text{S}_{53}$ . The finely powdered mineral is slowly decomposed by digestion with hydrochloric or nitric acid, with separation of some sulphur. It is readily decomposed by fusion with alkali carbonates and nitrate, and the solution gives with the Marsh test a characteristic germanium mirror. Germanium was also detected in cylindrite from Bolivia by this method. A rough separation of germanium and antimony was effected by carefully acidifying with dilute sulphuric acid the solution of the sulphides in sodium sulphide, the bulk of the germanium remaining in solution whilst antimony was precipitated. L. J. S.

**Minerals from Tsumeb, S.W. Africa.** O. PUFAHL (*Centr. Min.*, 1920, 289—296).—Zinciferous tennantite, occurring either alone (anal. I,  $D\ 4.61$ ) or intimately associated with galena (II), is massive, with black colour and greenish lustre and a dark cherry-red streak.

	S.	As.	Sb.	Cu.	Zn.	Pb.
I.	23.35	17.94	4.66	43.60	9.24	0.22
II.	22.65	19.65	4.03	43.19	9.27	0.08
	Fe.	Ag.	Au.	$\text{SiO}_2$	Total.	
I.	0.03	0.11	0.01	0.97	100.13	
II.	0.17	n.d.	n.d.	0.81	99.85	

Mimetite occurs in the secondary zone as compact masses and as almost colourless, prismatic crystals (anal. III); it is frequently altered to bayldonite. Mottramite is abundant as compact or cellular masses with sometimes a reniform (IV) or botryoidal (V) surface. It is dark olive-green, with a pale yellow streak, and is readily soluble in hot dilute hydrochloric acid with evolution of chlorine. Full details of the method of analysis are given; the results agree with  $4(\text{Cu,Pb})\text{O}, \text{V}_2\text{O}_5, 2\text{H}_2\text{O}$ , in which  $\text{Cu}:\text{Pb}=1:1$ . Cuprodesclowitzite as crusts of small, dark olive-green crystals showing pyramidal points gave VI, corresponding with  $4(\text{Cu,Pb})\text{O}, \text{V}_2\text{O}_5, \text{H}_2\text{O}$ , in which  $\text{PbO}:(\text{CuO}+\text{ZnO})=1:1$ . A new lead copper arsenate, named *duftite*, forms pale olive-green crusts of small, indistinct crystals (resembling olivenite in form) on crystals of azurite. It is soluble in hot dilute hydrochloric acid. Anal. VII corresponds with  $2\text{Pb}_3(\text{AsO}_4)_2, \text{Cu}_3(\text{AsO}_4)_2, 4\text{Cu}(\text{OH})_2$ . The mineral contains no trace of chlorine or phosphoric acid, and consequently it has probably not been derived from mimetite, although it is sometimes associated with remains of this.

	PbO.	CuO.	ZnO.	MnO.	$\text{V}_2\text{O}_5$ .	$\text{As}_2\text{O}_5$ .	$\text{SiO}_2$ .	$\text{H}_2\text{O}$ .	Total.	Sp. gr.
III.	67.31	trace	—	—	—	23.12	—	—	99.76*	6.98
IV.	54.70	18.75	0.19	trace	21.05	1.25	0.28	3.93	100.15	5.93
V.	53.33	19.50	0.16	trace	19.20	3.04	0.70	3.92	99.85	5.90
VI.	54.90	16.27	3.51	trace	21.69	1.36	0.07	2.33	100.13†	6.19
VII.	50.10	19.32	0.46	—	—	26.01	0.44	2.73	99.81‡	6.19

\* Incl.  $\text{PbCl}_2$  9.33 (Cl 1.38). † Also  $\text{Fe}_2\text{O}_3$  trace. ‡ Incl.  $\text{CaO}$  0.75

L. J. S.

**Phosphate-bearing Pegmatites from Bavaria.** H. LAUBMANN and H. STEINMETZ (*Zeitsch. Kryst. Min.*, 1920, **55**, 523—586).—Phosphate-bearing pegmatites, similar to those near Limoges in France and Branchville in Connecticut, are described from five localities in Bavaria. The anhydrous phosphate minerals, fluormanganapatite, triplite, triphylite, and triploidite, are present as original constituents of the pegmatite, and by their alteration by thermal waters they have given rise to a great variety of well-crystallised hydrated phosphate minerals. The latter include the iron (ferrous and ferric) phosphates, dufrenite, beraunite, strengite, phosphosiderite, cacozenite, and vivianite; manganiferous phosphates containing also iron and alkaline earths, such as fairfieldite, phosphophyllite, phosphoferrite, xanthoxenite, and kreuzbergite; rarely manganese ferrous phosphates of the heterosite-purpurite series; simple manganese phosphates are here, however, absent. Analyses are given of the following: I, altered triplite from Plössberg; the fresh material contains  $\text{P}_2\text{O}_5$ , 34.13%. II, triplite from Pleystein. III, triplite from Hagendorf. IV, triphylite from Hagendorf. V, strengite as good violet-blue crystals ( $a:b:c=0.8663:1:0.9776$ ) from Pleystein; formula  $\text{Fe}_2\text{O}_3, \text{P}_2\text{O}_5, 8\text{H}_2\text{O}$ . VI, phosphosiderite as almond-blossom-red crystals ( $a:b:c=0.5456:1:0.8905$ ) from Pleystein; formula  $\text{Fe}_2\text{O}_3, \text{P}_2\text{O}_5, 7\text{H}_2\text{O}$

VII, *phosphophyllite*, a new species, forming colourless or pale blue, monoclinic crystals ( $a:b:c=1.0381:1:1.7437$ ,  $\beta=89^{\circ}32'$ ) with

	P <sub>2</sub> O <sub>5</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	Li <sub>2</sub> O.	F.	Insol.	H <sub>2</sub> O.	Total.
I.	19.73	—	41.60	31.03	—	6.28	1.03	—	—
II.	33.14	—	33.51	25.42	—	6.77	0.46	—	—
III.	31.89	—	35.50	28.66	—	7.29	0.83	—	—
IV.	44.43	—	35.06	11.40	8.59	—	0.60	—	—
V.	38.24	43.40	—	—	—	—	—	18.89	100.53
VI.	37.71	44.38	—	—	—	—	—	17.31	99.40

perfect micaceous cleavage, D 3.081, from Hagendorf; formula  $P_2O_5, 2\frac{1}{2}R''O, \frac{1}{2}K_2O + \frac{2}{3}SO_4Al-OH + 3H_2O$  or  $3R_3P_2O_8 + 2AlOH\cdot SO_4 + 9H_2O$ .

VIII, *phosphoferrite*, a new species, from Hagendorf, occurring as cloudy-white or greenish, crystalline masses with greasy lustre,

	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Ign.	Insol.	Total.
VII.	25.85	9.17	6.12	13.55	5.12	12.04	8.50	13.17	3.66	98.09*
VIII.	35.10	0.75	0.61	40.35	5.30	6.20	0.55	4.67	1.94	— †

\* Including BaO 0.91. † Also MnO 2.46, Na<sub>2</sub>O 0.25, SiO<sub>2</sub> 1.03.

D 3.156. Formula  $H_3PO_4, 3PO_4, 4\frac{1}{2}R''$  or  $H_6R_0''(PO_4)_8$ . The primary apatite contains P<sub>2</sub>O<sub>5</sub> 42.61, MnO 4.93, and no chlorine, and is therefore described as *fluormanganapatite*. *Kreuzbergite*, a new species from the Kreuzberg at Pleystein, forms small, colourless to pale yellow, orthorhombic crystals ( $a:b:c=0.3938:1:0.5261$ ), D 2.139, and consists essentially of hydrated aluminium phosphate with some iron, calcium, and manganese. *Xanthoxenite*, a new species from Rabenstein, occurring as small, wax-yellow, monoclinic crystals, D 2.844, intimately associated with dufrenite and caxoxenite; it is a basic ferric phosphate (P<sub>2</sub>O<sub>5</sub>, 32.61; loss on ignition, 16.10%) with some manganese and calcium. L. J. S.

**Pickeringite from Opálbánya, Hungary.** VIKTOR ZSIVNY (*Zeitsch. Kryst. Min.*, 1920, 55, 629—631).—Yellowish-white, fibrous material with silky lustre gave (also traces of MnO, Na<sub>2</sub>O, NH<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>):

SO <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MgO.	CaO.	FeO.	H <sub>2</sub> O.	Total.
36.62	9.52	4.04	4.06	0.70	0.23	45.42	100.59

agreeing with the usual formula,  $(Al,Fe)_2(Mg,Ca,Fe)(SO_4)_4, 22H_2O$ . Together with other sulphates, the mineral is of recent formation in the levels of the opal mines, having been formed by the decomposition of the small crystals of iron-pyrites present in the hypsitherne-andesite matrix of the opal. L. J. S.

**Minerals from Madagascar and the Urals.** RENÉ CHARLES SABOT (*Thèse, Univ. Genève*, 1914, 1—138; from *Jahrb. Min.*, 1920, i, Ref. 138—142).—Crystallographic and optical determinations, usually with analyses, are given for a number of minerals. Most of the data have been previously published (Duparc, A., 1910. ii, 221; 1913, ii, 782; 1914, ii, 664, etc.), but the following

analyses appear to be new. I, Muscovite, plumose mica, from Ampatsakana, Madagascar. II, Spessartite crystals from Takovaya, Urals. Blue apatite, occurring with rubellite and feldspar at Antsongombato, Madagascar, gave:  $P_2O_5$ , 40.09; CaO, 54.45; MnO, 1.80; Cl, 0.20; F [3.46]; D 3.2013.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.
I.	44.35	37.40	—	5.30	0.30	0.19
II.	35.12	20.40	2.06	6.78	33.16	2.10

	MgO.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.	Sp. gr.
I.	1.67	5.94	5.29	100.44*	2.8908
II.	0.15	—	—	99.77	4.1577

\* Also TiO<sub>2</sub>, Na<sub>2</sub>O traces.

L. J. S.

**Optical Characters of Epidote.** M. GOLDSCHLAG (*Tsch. Min. Mitt.*, 1917, **34**, 23—60; from *Jahrb. Min.*, 1920, i, Ref. 135—137).—Optical determinations were made on clinozoisite and epidote from various localities, and the results correlated with the chemical composition (percentage of ferric iron reckoned as an iron-epidote molecule). The following new analysis, by KAROLINE LUDWIG, is given of epidote from Pfarrerb, Zöptau, Moravia:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	H <sub>2</sub> O.	Total.
38.34	26.11	9.67	1.07	23.93	0.34	n.d.	99.46

L. J. S.

**Andesine from Hohenstein, Kremsthal, Lower Austria.** O. GROSSPIETSCH (*Sitzungsber. Akad. Wiss. Wien*, 1918, **127**, 439—447; from *Jahrb. Min.*, 1920, i, Ref. 132).—Analysis of crystals gave:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Na <sub>2</sub> O.	Ign.	Total.	Sp. gr.
59.98	24.67	0.54	7.26	trace	7.36	0.09	99.90	2.67

corresponding with Ab<sub>65</sub>An<sub>35</sub>. The optical constants are given.

L. J. S.

### Analytical Chemistry.

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**Qualitative Chemical Analysis.** V. MACRI (*Boll. Chim. Farm.*, 1920, **59**, 385—389).—The author gives a scheme according to which the metals are detected approximately in the opposite order to that of the method commonly employed, one advantage of this procedure being that it allows of the use of fixed alkalis or their salts. [See *J. Soc. Chem. Ind.*, 1920, November.]

T. H. P.

**The Analysis of Aqueous Solutions with the Aid of the Refractometer.** MAX DE CRINIS (*Zeitsch. physiol. Chem.*, 1920, 110, 254—265).—The refractive index of salt solutions which do not manifest the phenomenon of molecular attraction is in direct linear proportion to the percentage of the concentration of the salt in the solution. On establishing this relation between the refractive index and the concentration of a solution, it is possible to calculate the percentage of the concentration by means of the formula  $y = (nDX\% - 1.33320)/b$  ( $nDX\%$  = refractive index of  $X\%$  solution,  $b$  = refractive index of 1% solution of the same salt, 1.33320 = refractive index of distilled water). The refractive index of a mixture of equal parts of various salt solutions is equal to the sum of the refractive indices of the solutions which make it up. If by mixing these salts some substance is precipitated, the refractive index of the precipitated salt can be obtained by subtracting the refractive index of the remaining solution from the sum of the refractive indices of the component solutions. The ion content of the aqueous solution can therefore be calculated, as follows:  $P = (nDRX\% - nDOX\%)/K$ .  $P$  = percentage;  $nDRX\%$  = refractive index of  $X\%$ -solution obtained by calculation;  $nDOX\%$  = refractive index observed after precipitation;  $K = nDR1\% - nDO1\%$  of a 1% solution. S. S. Z.

**A Simple Method for Titrating Electrometrically to a Desired End-point in Acid-alkaline Reactions.** P. E. KLOPSTEG (*Science*, 1920, 52, 18—19).—The hydrogen electrode can be utilised to compare a known standard solution with one of unknown  $p_H$  value. From the curves of Sørensen (*Ergebn. Physiol.*, 1912, 12, 393) or the formulæ of Clark and Lubs (*A.*, 1916, ii, 44) is selected the solution with  $p_H$  value corresponding with the point to which it is desired to titrate. This solution is placed in connexion (by means of a bridge of potassium chloride solution) with the unknown, each being provided with a hydrogen electrode. The two electrodes are connected by a tapping key and high-resistance galvanometer. Titration to an end-point is effected by merely adding solution until, on tapping the key, no deflection is observed, showing equal hydrogen-ion concentrations in the two solutions. The accuracy is limited by that of the  $p_H$  value of the standard solution. CHEMICAL ABSTRACTS.

**The H-ion Concentration of some Standard Solutions at Various Temperatures.** L. E. WALBUM (*Biochem. Zeitsch.*, 1920, 107, 219—228; *Compt. rend. Soc. Biol.*, 1920, 83, 707—709).—The H-ion concentration of mixtures of glycine and sodium hydroxide, borate and hydrochloric acid, and borate and sodium hydroxide increases with increased temperature between 10° and 70°. The reverse is the case with a citrate and sodium hydroxide mixture. In the former three mixtures, the alteration is more marked in the alkaline mixtures, but diminishes with the diminution of the alkalinity of the mixtures S. S. Z.

**Use of Ethyl Ether in Iodometric Estimations.** L. GERET (*Mitt. Lebensmittelunters. Hyg.*, 11, 67—68; from *Chem. Zentr.*, 1920, iv, 354).—Commercial ethyl ether can liberate large quantities of iodine in consequence of the presence of peroxidised substances. Such ether should be dehydrated with calcium chloride and subjected to prolonged treatment with metallic sodium, or shaken with concentrated alkali thiosulphate, rapidly dried over calcium chloride, and distilled.  
H. W.

**Extensive Employment of Arsenious Acid in Volumetric Analysis.** R. NAMIAS (*Giorn. chim. ind. applicata*, 1920, 2, 176).—A reply to de Bacho (this vol., ii, 188).

CHEMICAL ABSTRACTS.

**Application of the Thermal Conductivity Method to the Analysis of Complex Mixtures of Gases.** E. R. WEAVER and P. E. PALMER (*J. Ind. Eng. Chem.*, 1920, 12, 894—899).—The thermal conductivity method can only be applied quantitatively when the probable identity and amounts of constituents likely to be present in a gaseous mixture are known. For estimation of a constituent by comparison with a standard gas, air is the most suitable standard for mixtures with low conductivity, and hydrogen for those with high conductivity. This is suitable for estimating hydrogen in air, the relative proportions of hydrogen and ammonia in gases for synthetic ammonia processes, and impurities in hydrogen. In other cases, such as the estimation of chlorine, hydrogen chloride, sulphur dioxide, acetylene, and water vapour in various gaseous mixtures, the results are calculated by comparing the conductivities before and after a chemical reaction. Thus, the total amount of atmospheric gases in a hydrogen-filled balloon may be estimated by applying the method before and after the reaction of the oxygen with the hydrogen. Similarly, methane in air may be estimated by the difference in the results obtained before and after passing the air over hot copper oxide. Another modification is to add a gas to a mixture prior to the reaction. For example, in estimating oxygen in flue gas, hydrogen is first added, and the oxygen removed by combustion. The difference in the conductivities of the residual excess of hydrogen and nitrogen in the mixture is too small to affect the accuracy of the results for oxygen. In like manner, successive combustions with oxygen and hydrogen may be used for certain mixtures, as, for example, in estimating carbon monoxide in the presence of large amounts of hydrogen.  
C. A. M.

**Estimation of Chlorine in Blood.** M. RODILLON (*Presse méd.*, 28, 85—86; from *Chem. Zentr.*, 1920, iv, 315—316).—A solution of trichloroacetic acid (1:5; 15 c.c.) is added slowly and with stirring to an equal volume of the well-centrifuged serum, and the mixture is passed through a folded filter. 11.7 c.c. of the filtrate (a portion is reserved for the estimation of carbamide) are treated with *N*/10-silver solution (10 c.c.), distilled water

(50—60 c.c.), and finally with ferric alum solution (10 c.c.); the mixture is thoroughly agitated and titrated with *N*/10-ammonium thiocyanate solution until the red coloration persists. H. W.

**A New Method for the Estimation of Bromine.**

G. HARTWICH (*Biochem. Zeitsch.*, 1920, **107**, 202—206).—The urine is incinerated with sodium carbonate and acidified with sulphuric acid. Chlorine water is added and the liberated bromine is extracted with chloroform. The bromine is calculated from the quantity of chlorine used up. 347 Mg. of sodium bromide were estimated by this method in 100 c.c. of bromine-free urine with an error of about 3%. S. S. Z.

**Use of Barcroft's Differential Apparatus.**

R. WERTHEIMER (*Biochem. Zeitsch.*, 1920, **106**, 1—11).—Replacement of Barcroft's formula (A., 1908, ii, 319, 529) by that of Münzer and Neumann (A., 1917, i, 520) gives for the gas volume a value higher by about 0.5%, or, if the barometric pressure is corrected for the pressure of the water vapour, lower by about 0.4%. Use of Barcroft's formula and neglect of the water-vapour pressure correction is hence recommended. Determination of the constants of the apparatus is described. T. H. P.

**Investigations on Alveolar Gas Pressures by a New Method.**

PIUS SUPERSAXO (*Biochem. Zeitsch.*, 1920, **106**, 56—82).—The author has tested a new method, devised by Asher, for investigating alveolar air which permits of the estimation of both the carbon dioxide and the oxygen. The analysis is carried out by means of the Bunte burette, and as it requires 100 c.c. of air, Haldane and Priestley's method (A., 1905, ii, 400) is modified so as to yield increased quantities of the alveolar air. The method is fully described. T. H. P.

**Estimation of Neutral Sulphur in Urine.**

PAUL LIEBESNY (*Biochem. Zeitsch.*, 1920, **105**, 43—48).—Estimation of the sulphur in sulphosalicylic acid solution by precipitation as benzhidine sulphate was found to yield results 8—10% in excess of the true value, owing to the presence of sulphur compounds in the gas employed as source of heat during the operations. The author has therefore modified Raiziss and Dubin's method of estimating the total sulphur in urine (A., 1914, ii, 671), use being made of an electric combustion furnace. The total sulphates in urine may be estimated by Rosenheim and Drummond's method (A., 1914, ii, 485), the difference between total sulphur and total sulphates representing neutral sulphur. T. H. P.

**Volumetric Method for the Estimation of Acids and Bases which yield Insoluble Salts.**

HANS TH. BUCHERER (*Zeitsch. anal. Chem.*, 1920, **59**, 297—302).—For the estimation of sulphuric acid, the hot solution containing the latter is titrated with *N*-barium chloride until the precipitation of barium



sulphate appears to be complete. A small portion of the solution is then filtered, and the filtrate divided into two portions, which are tested with a drop of barium chloride solution and a drop of dilute sulphuric acid respectively. If a precipitate is obtained with barium chloride, the titration is continued, and the solution again tested after filtration. In this way, the amount of barium chloride necessary for the precipitation of the sulphuric acid is ascertained approximately. The titration is then repeated on a fresh portion of the original solution, the final titration being made with  $N/10$ -barium chloride solution. Similar methods of titration may be used for the estimation of calcium (as oxalate), magnesium (as ammonium magnesium phosphate), etc.

W. P. S.

#### **A Little-known Still-head for Kjeldahl Distillation.**

A. PRANGE (*Chem. Zeit.*, 1920, **44**, 681).—To guard against frothing over during distillation of ammonia when estimating nitrogen by the Kjeldahl process, the glass tube leading from the distillation flask to the receiver is inclined in an upward direction for some distance from the safety bulb. This gives additional security should the bulb become filled with froth.

E. H. R.

**The Technique for the Estimation of the Residual Nitrogen in Blood.** JOH. FEIGL (*Biochem. Zeitsch.*, 1919, **101**, 62—73).—A theoretical paper. Folin and Wu's method (A., 1919, ii, 308) is considered an improvement on other methods.

S. S. Z.

**Colorimetric Estimation of Ammonia, Nitrites, and Nitrates.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1920, **57**, 1253—1264).—In addition to the difficulty that colorimetric determinations are not accurate to within 5 to 10%, irregularities occur in practice from the influence of such factors as the quantity of reagent, the temperature, the time, the presence of retarding substances, etc. In the quantitative estimation of traces of ammonia by means of Winkler's reagent, which will detect 0.1 mg.  $\text{NH}_4$  per litre, time was not found of great importance, the colour being at its maximum for different concentrations of the reagents after fifteen minutes in all cases. The quantity of reagent used has a marked effect, 0.3 c.c. of Winkler's reagent producing the same colour with 50 c.c. of a solution containing 0.6 mg.  $\text{NH}_4$  per litre as 0.5 c.c. produced with the same volume of a solution containing 0.4 mg.  $\text{NH}_4$  per litre. The strongest colour was obtained by adding 0.5 c.c. of the reagent to 50 c.c. of the ammoniacal solution. The presence of excess of potassium iodide depresses the sensitiveness enormously; the presence of 0.3 c.c.  $N$ -KI with 1 c.c. of the reagent and 50 c.c. of a solution containing 10 mg.  $\text{NH}_4$  per litre reduced the colour to equality with that given by 50 c.c. of a solution containing 0.35 mg.  $\text{NH}_4$  with 1 c.c. of the reagent, whilst 0.6 c.c.  $N$ -KI prevented the formation of the colour completely. The influence of a small excess of potassium

iodide varies with the concentration of the reagents. Bromides and thiocyanates have a preventive effect, although not so great as iodides. Chlorides have very little effect unless in large quantity. Sulphates have little effect on the colour, but hasten the separation of the orange precipitate. Secondary phosphates weaken the colour, whilst addition of excess of alkali hydroxide inhibits it entirely, as also does cyanide. A very satisfactory reagent, capable of detecting 0.1 mg.  $\text{NH}_4$  per litre, is mercury sodium chloride in weak alkaline solution, which gives a white opalescence permitting of nephelometric estimation.

The recent work of Frederick (A., 1919, ii, 371) and Massink (*Water*, 3, 89) on the phenol-sulphuric acid method of estimating nitrates is examined, and the influence of traces of chlorides shown by Massink to be necessary is confirmed, although the quantitative effect is greater than Massink stated. The test is best carried out by adding to the working solution 0.5 c.c. *N*-NaCl, evaporating to dryness, adding to the residue 2 c.c. of phenol-sulphuric acid, and warming for twenty minutes on the water-bath. The liquid is then diluted and rendered ammoniacal according to the procedure of Frederick. In the new form, the reaction is quantitative, the colour being proportional to the amount of nitrate present. Nitrites have very little effect on the reaction in this form. The brucine-sulphuric acid method was also examined, but no quantitative results could be obtained.

The Griess-Romijn method for the colorimetric determination of nitrite is also examined, and modifications are recommended. If 100 c.c. of the reagent be added to 50 c.c. of the solution under test, and the mixture warmed to 55–60° for five minutes, the maximum colour is reached at once on cooling. Since alkalis inhibit strongly, a hard water should first be made acid with acetic acid.

S. I. L.

**Estimation of Ammonia in Urine, in Serous Liquids, and in the Oxidised Liquid of the Kjeldahl Method.** ARNOLD HAHN and ELISABETH KOOTZ (*Biochem. Zeitsch.*, 1920, 105, 220–228).—Using Hahn's modification of the Krüger, Reich, and Schittenhelm method, all the ammonia is expelled in five minutes from a solution containing 0.04 gram of ammonia as ammonium sulphate, 25 c.c. of water, 10 grams of sodium chloride, 1 gram of sodium carbonate, and 30 c.c. of 96% alcohol if the distillation flask is heated in a boiling-water bath and the distillation is carried out in the maximum vacuum given by a water pump. Under these conditions, carbamide (2 grams) yields no ammonia. Cooling of the receiver containing the standard acid for absorbing the ammonia is found to be unnecessary. Methods based on the above results are given for the estimation of ammonia in urine either free from, or containing, protein, in blood serum, and in the decolorised acid liquid of the Kjeldahl method. A special indicator containing sodium alizarinsulphonate and methylene-blue is used for titrating the alcoholic *N*/100-acid used in the case of blood serum.

T. H. P.

**The Conductometric Titration of Phosphoric Acid and its Salts.** I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, **112**, 165—171).—Phosphoric acid behaves as a strong acid, and cannot be titrated conductometrically in concentrated solution (compare this vol., ii, 420). In dilute solution it can be titrated in exactly the same way as a mono- or di-basic acid, the first equivalent point being very sharp, the second less distinct. The conductometric method of titration has the advantage over the indicator method that indicators give indistinct end-points in very dilute solutions of phosphoric acid. Secondary phosphates, for example,  $\text{Na}_2\text{HPO}_4$ , can be titrated with acids when the concentration is less than 0.01 molar. When the concentration is greater, the break in the conductivity curve at the point corresponding with primary phosphate is indistinct, owing to the dissociation of phosphoric acid. Secondary phosphates cannot be titrated with alkali, on account of the hydrolysis of the tertiary phosphates. Dilute solutions of pyrophosphates can be satisfactorily titrated with acid to the secondary salt. The break corresponding with the tertiary salt is indistinct.

E. H. R.

**Estimation of Carbon Dioxide in Alkali Hydrogen Carbonates in the Presence of Carbonates.** WILHELM HARTMANN (*Zeitsch. anal. Chem.*, 1920, **59**, 289—297).—When a mixture of sodium hydrogen carbonate and sodium carbonate is mixed with 70% glycerol solution (7 c.c. for each 0.1 gram of carbonate) and heated at  $115^\circ$  for ten minutes, the whole of the carbon dioxide in the hydrogen carbonate is liberated, and, after being passed through suitable drying apparatus, may be collected in an ordinary potash bulb and weighed. At the end of the ten minutes the temperature should be lowered to  $100^\circ$ , and a current of air passed through the apparatus to convey the carbon dioxide into the potash bulb. If the same mixture is then heated at  $190^\circ$  for five minutes, two drops of water now added, and the heating continued for a further ten minutes, the carbonate is decomposed, and the resulting carbon dioxide may be collected and weighed. In most cases, the greater part of the water evolved with the carbon dioxide may be separated by means of a short reflux apparatus, but when ammonium salts are present, a vessel containing sulphuric acid must be used for drying the gas and removing the ammonia.

W. P. S.

**The Conductometric Estimation of Carbonic Acid and its Salts.** I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, **112**, 155—164).—Solutions of carbonic acid, from 0.0015 to 0.02 mol. in strength, can be titrated conductometrically with alkali. The conductivity straight-line curve becomes steeper after the formation of the hydrogen carbonate, and again steeper after the formation of the normal carbonate. The breaks in the curve, however, are not sharp, especially in very dilute solutions, in which, owing to the considerable hydrolysis of the carbonate, the

straight-line portions become rounded into a continuous curve. The sharpness of the titration can be greatly increased by having present an excess of calcium salt (calcium chloride) to precipitate the carbonate as it is formed. Time must be allowed during the titration for the precipitation of the calcium carbonate.

Carbonic acid cannot be titrated with carbonate to the hydrogen carbonate conductometrically, because the angle between the two portions of the curve is too obtuse. On the other hand, carbonate can be titrated with acid. According to the dilution, the conductivity may fall (in dilute solution) or rise (in stronger solutions, above 0.1*N*) up to the hydrogen carbonate point. From this point, which is not sharp, to the neutral point, the conductivity increases gradually, and at the neutral point there is a sharp rise. The neutral point is very sharp in extremely dilute solutions. Free alkali hydroxide can be estimated in presence of carbonate by titration with acid if not present in too small an amount. The amount of hydrogen carbonate in carbonate can be determined by titration with alkali or acid, but its amount must not be too small, or the direction of the corresponding portion of the curve cannot be determined with sufficient accuracy. A very weak acid, such as boric acid, can be titrated in presence of sodium carbonate with alkali hydroxide with satisfactory results. E. H. R.

**Microchemical Reactions of Radium ; its Differentiation from Barium by Iodic Acid.** G. DENIGÈS (*Compt. rend.*, 1920, 171, 633—635).—Radium salts give results identical with those of barium salts in the microchemical tests where hydrofluosilicic acid, oxalic acid, tartaric acid, potassium ferrocyanide, potassium tartrate, ammonium cyanurate, or ammonium phosphomolybdate in ammoniacal solution are used respectively as reagents. Iodic acid can be used, however, under certain conditions to differentiate between the salts of these two metals. If the concentration of the solution does not exceed 0.3%, radium and barium salts give typical and distinct microcrystalline precipitates with a 10% solution of iodic acid. W. G.

**Titration with Surface-active Substances as Indicators.**  
**II. Estimation of Acidity with Capillary-active Substances of Alkaline Nature.** WILHELM WINDISCH and WALTHER DIETRICH (*Biochem. Zeitsch.*, 1919, 100, 130—147. Compare this vol., ii, 48).—Salts of substances of an alkaline nature, such as quinine hydrochloride, veratrine hydrochloride, eucupine dihydrochloride, were used as indicators in acidimetric titrations, according to Traube's method, by changing the surface tension of the indicator. Eucupine dihydrochloride was found to be as sensitive as decolic acid is in alkalimetry. With this indicator, it is possible to carry out graduated titrations of a strongly dissociated acid in the presence of a primary phosphate in varying proportions. By this method, the amphoteric reaction of mixtures of primary and secondary phosphates can also be demonstrated. S. S. Z.

**Titration with Surface-active Substances as Indicators.**

**III. Investigation of Carbonates and Phosphate-Carbonate Mixtures by Utilising Surface-active Indicators of Acid and Alkaline Nature.** WILHELM WINDISCH and WALTHER DIETRICH (*Biochem. Zeitsch.*, 1919, **101**, 82—109. Compare this vol., ii, 48, and preceding abstract).—The carbonates and hydrogen carbonates of potassium and sodium react alkaline with eucupine dihydrochloride as a surface tension indicator; those of magnesium react less alkaline than the above, but more alkaline than calcium normal and hydrogen carbonates. When these carbonates are mixed with primary potassium phosphate in the cold, the two substances react until a certain equilibrium is attained, showing the same order of alkalinity as the above. This is obtained with the alkaline surface tension indicator, eucupine dihydrochloride, as well as with the acid surface tension indicator, sodium undecoate. When heated, the alkali carbonates have the same influence on the primary phosphate as alkali hydroxide. The action of magnesium and calcium hydrogen carbonates on the primary phosphate under these conditions is complicated. The alkaline action of the alkaline earth hydrogen carbonates is proportionately greater when small quantities are used than when larger ones are employed.

S. S. Z.

**Estimation of Potassium as Perchlorate, and the Separation from Sodium, etc.** R. LEITCH MORRIS (*Analyst*, 1920, **45**, 349—368).—A critical examination of the perchlorate method for the estimation of potassium, together with suggestions as to the most suitable forms of apparatus. The potassium salt solution should be evaporated three times with perchloric acid, and in the final evaporation taken practically to dryness. The residue is treated with 10 c.c. of wash liquid (100 c.c. of 98% by vol. alcohol and 1 c.c. of 20% perchloric acid), stirred occasionally for fifteen minutes when sodium is present and the liquid then decanted through a weighed Gooch crucible containing asbestos. When only potassium is present, the precipitate is rinsed directly on to the filter with a small, measured quantity of the wash liquid. If sodium is present, the basin containing the precipitate from the first decantation is heated slightly to evaporate the alcohol, the precipitate dissolved in a small quantity of water, the solution evaporated to dryness, the precipitate treated with 10 c.c. of wash liquid, the latter decanted on to the filter, and the precipitate transferred by using 10 c.c. of the filtrate. Finally, the precipitate is washed on the filter by a measured volume of wash liquid, the crucible and its contents dried at 130° to 150° for one hour, cooled in a desiccator for one hour, and weighed. The weight is taken as being constant when, on washing with 3 c.c. of liquid, the difference between successive weighings does not exceed 0.2 mg. When much phosphoric acid is present, the evaporation with perchloric acid should not be to dryness, but to a moist, pasty condition; the residue is then treated with 15 c.c. of 98% alcohol, and finally washed with the wash liquid. Calcium, iron,

aluminium, and barium do not interfere, and magnesium is also without effect provided that the evaporation with perchloric acid is not carried to dryness. Organic acids tend to char during the evaporation, and when they are present it would seem preferable to separate the potassium previously by the cobaltinitrite method. In the case of sulphates, the sulphuric acid should be removed by treatment with barium chloride, but it is not necessary to remove the slight excess of barium chloride used.

W. P. S.

### **The Precipitation of the Calcium Group and Magnesium.**

I. M. KOLTHOFF (*Pharm. Weekblad*, 1920, **57**, 1229—1234).—The sensitiveness of ammonium carbonate, as usually used for the precipitation of Group IV in presence of ammonium chloride, leaves much to be desired. Ammonium carbonate in the cold gives no precipitate with solutions containing less than 25 mg. of calcium per litre, and at that concentration the precipitate is visible only after fifteen minutes. The sensitiveness is greater at the boiling point; in presence of free ammonia, a concentration of 5 mg. of calcium per litre, shows a precipitate in boiling ammoniacal solution. Ammonium chloride renders the reaction much less sensitive. The same conclusions are found to hold for strontium and barium, the latter being least sensitive to ammonium carbonate, as would be expected from the solubilities of the Group IV metal carbonates.

Sodium carbonate is found to be a much more sensitive reagent, giving precipitates at the boiling point from solutions containing only 1 mg. of calcium, 3 mg. of strontium, or 5 mg. of barium per litre. The use of sodium hydroxide and carbonate together is recommended to ensure complete precipitation of magnesium, which can be removed by the chromate method and reprecipitated with ammonium phosphate. Considerable excess of these reagents is not harmful to the reaction, as the ammonia set free from the ammonium chloride present has no tendency to prevent precipitation of the magnesium.

S. I. L.

**Estimation of Calcium and Magnesium in Different Saline Solutions.** E. CANALS (*Compt. rend.*, 1920, **171**, 516—518).—If to a solution containing calcium, magnesium, iron, and aluminium salts, just acidified with sulphuric acid, sodium phosphate is added and the solution made alkaline with ammonium hydroxide, it is possible to retain the whole of the calcium and magnesium in solution by acidifying with acetic acid and shaking vigorously for several minutes.

W. G.

**Detection of Magnesium.** FRITZ EISENLOHR (*Ber.*, 1920, **53**, [B], 1476—1477).—Five c.c. of a solution of alkannin in alcohol (96%) are treated with a drop of 2*N*-ammonium carbonate solution, which does not cause any change in colour, and then with a drop of the neutral salt solution; the presence of magnesium, strontium, or manganese is denoted by the development of a bluish-violet coloration which becomes pale red after acidification with one or at most two drops of 2*N*-hydrochloric acid; subsequent addition of the

same number of drops of 2*N*-ammonium carbonate solution restores the bluish-violet colour only if magnesium is present. If the latter is present as magnesium ammonium phosphate, the salt is dissolved in 2*N*-hydrochloric acid, and a drop of this solution is added to the alkannin tincture; further addition of 1—2 drops of ammonium carbonate causes the appearance of the bluish-violet colour if magnesium is actually present, whilst otherwise the original colour of the tincture is restored. It is essential that the alcoholic solution should not become diluted with water, since in this case the ammonia hydrolytically produced gives a blue coloration. H. W.

**The Acidimetric Estimation of Heavy Metals in their Salts.** I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, 112, 172—186).—Experiments were made to determine with what degree of accuracy the salts of heavy metals which form insoluble hydroxides can be titrated with alkali hydroxides, either by the conductometric method or with the help of indicators. The statement of Harned (A., 1917, ii, 272) that magnesium sulphate can be estimated conductometrically by titration with barium hydroxide was confirmed. Satisfactory results were also obtained by precipitating the magnesium hydroxide with excess of standard alkali, filtering, and titrating back with standard acid. The conductometric method gave unsatisfactory results when zinc sulphate was titrated with sodium or barium hydroxide, owing to the precipitation of basic salt. Better results were obtained by titrating sodium hydroxide with zinc sulphate. In the case of copper sulphate also, the formation of basic salt interferes with the titration, and satisfactory results could not be obtained. Mercuric chloride can be titrated conductometrically with accuracy by running the solution into sodium hydroxide solution, which should not be stronger than 0.01*N*. In the case of aluminium salts, when these are titrated with sodium or barium hydroxide, a sharp break in the conductivity curve is not obtained at the neutral point, but there is a very sharp break at the point where the formation of aluminate is complete. Aluminium hydroxide behaves, therefore, as a mono-basic acid. Aluminium sulphate or alum can be titrated with sodium hydroxide at the boiling temperature in presence of excess of barium nitrate, using phenolphthalein as indicator. Slight excess of alkali is run in and titrated back with acid. The results are accurate.

E. H. R.

**Use of Diphenyl Derivatives in Qualitative Analysis.** F. FEIGL (*Chem. Zeit.*, 1920, 44, 689—690).—Benzidine and other diphenyl derivatives yield intense blue colorations with manganic, ceric, cobaltic, and thallic compounds. For the detection of traces of the latter their solution is rendered alkaline with sodium hydroxide solution prepared with ordinary tap water (the presence of calcium carbonate is advantageous since it occludes the traces of metallic hydroxides), the mixture filtered, and the filter then treated with a drop of benzidine acetate solution. The test will detect the presence of 1 part of manganese in 125 million parts of

solution. Thallic compounds even give a blue coloration with the reagent without previous treatment with alkali; cobalt salts must be heated with alkali solution to obtain the pink hydroxide before the reaction with benzidine can be obtained. In the case of iron the blue coloration is not obtained when all the iron has been precipitated from solution by alkali.

W. P. S.

**Electro-analytical Separation of Nickel (Cobalt) from Arsenic.** N. HOWELL FURMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 1789—1793).—Nickel may be quantitatively separated from salts of arsenic acid in ammoniacal solution by the electric current. Cobalt on deposition carries down arsenic, whereas the nickel precipitate is free from arsenic. If the two metals are deposited simultaneously, arsenic may or may not be deposited, according to the conditions.

J. R. P.

**Volumetric Methods for Estimating Tin.** J. G. F. DRUCE (*Chem. News*, 1920, **121**, 173—175).—Stannous tin may be more accurately estimated by a volumetric method in an acid solution. Titration with standard iodine solution in the presence of hydrochloric acid gives satisfactory results with stannous chloride, inorganic stannochlorides, and stannochlorides of aliphatic amines, but is less suitable for aromatic amine compounds, which have a tendency to darken during the titration, and so obscure the end-point. For the titration of stannous chloride with potassium permanganate solution, the hydrochloric acid should be kept as low as possible by dissolving the salt in dilute sulphuric acid, and titrating the solution as rapidly as possible. Potassium dichromate is usually less trustworthy as a reagent for the titration.

C. A. M.

**Estimation of Zirconium.** MELVIN S. SMITH and C. JAMES (*J. Amer. Chem. Soc.*, 1920, **42**, 1764—1770).—Zirconium is precipitated by selenious acid from a boiling solution acidified with hydrochloric acid. The basic selenite on ignition leaves zirconia. It is shown that this method gives satisfactory results in the estimation of zirconium in a pure salt, in the separation of zirconium from aluminium and rare earths, and from iron when the amount of ferric oxide in the combined oxides of iron and zirconium does not exceed 10%. Titanium is precipitated with zirconium, and a correction must be applied in this case or the precipitation carried out in presence of excess of hydrogen peroxide, when zirconium alone is precipitated. If phosphates are present the zirconium phosphate in the ammonia precipitate is insoluble in hydrochloric acid, and must be fused with sodium carbonate, boiled with water, and the residue dissolved in hydrochloric acid and added to the main solution. A method for the analysis of zirconia ore is described.

J. R. P.

**Estimation of Antimony in Lead-Antimony Alloys.** L. BERTIAUX (*Ann. Chim. anal.*, 1920, [ii], **2**, 273—278; *Bull. Soc. chim.*, 1920, [iv], **27**, 769—771; *Chim. et Ind.*, 1920, **4**, 467—472).

The alloy is dissolved by heating with sulphuric acid and



sodium sulphate, the solution is diluted with water, hydrochloric acid, and a few drops of a 0.1% solution of Poirrier's orange, and the mixture is titrated with standardised permanganate solution until the colour is just discharged. The hydrochloric acid keeps the antimony sulphate in solution, and as soon as all the antimony has been oxidised by the permanganate the next drop of permanganate solution introduced reacts with the hydrochloric acid, liberating chlorine, which decolorises the Poirrier's orange. Bismuth, copper, tin, and arsenic do not interfere; iron is titrated together with the antimony, but its quantity may be estimated colorimetrically with thiocyanate in the solution in which the antimony has been titrated. [See, further, *J. Soc. Chem. Ind.*, 1920, 693A.] W. P. S.

### **Sensitive Modification of Lieben's Reaction for Iodoform.**

RUDOLF KUNZ (*Zeitsch. anal. Chem.*, 1920, **59**, 302—303).—For the detection of traces of alcohol by this test, 10 c.c. of the solution are treated with 2 c.c. of 10% sodium hydroxide solution, 0.15 gram of potassium iodide and 0.2 gram of potassium persulphate, and the mixture is heated at 60°. A solution containing one drop of alcohol in 100 c.c. of water yields a turbidity, due to the formation of iodoform, within ten minutes. W. P. S.

**The Conductometric Titration of Phenols.** I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, **112**, 187—195).—Phenol and the cresols can be accurately titrated conductometrically with alkali in 0.1 or 0.01*N*-solution. Vanillin and sodium phenolsulphonate can be similarly titrated. In salicylic acid the hydroxyl group loses its acidic character and cannot be titrated, but its esters, for example, salol or methyl salicylate, can be accurately titrated as phenols; *p*-hydroxybenzoic acid behaves as a dibasic acid. Thymol and  $\beta$ -naphthol are also satisfactorily titrated. Of the dihydroxybenzenes, catechol behaves as a monobasic acid, the conductivity curve showing only one break, corresponding with the first hydroxyl group; quinol behaves as a dibasic acid, the first break not being very distinct, whilst resorcinol, which also behaves as a dibasic acid, gives better results when titrated with barium instead of sodium hydroxide. Pyrogallol functions as a dibasic acid, not monobasic, as stated by Thiel and Roemer (*A.*, 1908, i, 787, 791), and so does phloroglucinol, whilst gallic acid, having a carboxyl in addition to three hydroxyl groups, behaves as a tribasic acid.

E. H. R.

**Estimation of Terpin.** OBDULIO FERNÁNDEZ and N. LUENGO (*Anal. Fis. Quim.*, 1920, **18**, 158—165).—When terpin is treated with acetic anhydride and anhydrous sodium acetate, only one of its two hydroxyl groups is acetylated; hence it behaves like a monohydric alcohol, although the results are slightly high. When a small quantity of sulphuric acid is used instead of sodium acetate, the reaction takes place spontaneously, and one hydroxyl group is acetylated. The quantity of acetic anhydride required is two to three times that of the terpin, the mixture being left for

one or two hours. Complete esterification is achieved by Boulez's method (A., 1907, ii, 306): 5 grams of terpin are dissolved in 25 grams of rectified oil of turpentine and 40 grams of acetic anhydride. Three grams of fused sodium acetate are added, and the mixture boiled for three hours. The liquid is digested for twenty minutes on the water-bath with a little water, and a saturated salt solution added; the top layer is made up to 100 c.c. with oil of turpentine and dehydrated with calcined sodium sulphate; an aliquot part of the liquid is then hydrolysed with alcoholic  $N/2$ -sodium hydroxide solution. W. R. S.

**An Accelerated Method of Estimating the Reducing Values of Cellulosic Substances.** E. KNECHT and L. THOMPSON (*J. Soc. Dyers and Col.*, 1920, **36**, 255—257).—Schwalbe's method for estimating the copper number of oxycellulose is modified by adding the cuprous oxide to a ferric salt solution and titrating the ferrous salt so formed with potassium permanganate. By this means it is unnecessary to determine the unreduced copper absorbed by the cellulose (copper hydroxide number), which is the difference between the above number and that obtained from an estimation of the unreduced copper in the filtrate by titanous chloride.

The copper number may be determined by a process based on the fact that oxycellulose precipitates cuprous thiocyanate from solutions of the cupric salt. This method avoids the errors that the action of the alkali hydroxide in Fehling's solution on oxycellulose may cause.

The copper number may also be determined by heating oxycellulose with sodium hydroxide and rosinduline, and then titrating with titanous chloride to determine the amount of dye reduced.

All three methods give sufficiently accurate results, and are more quickly carried out than the original Schwalbe method. [See *J. Soc. Chem. Ind.*, 1920, 718A.] A. J. H.

**Estimation of Acetic Anhydride.** KNUT WOLGAST (*Svensk Kem. Tidskrift*, 1920, **32**, 110).—Twenty-five c.c. of acetic anhydride are dissolved in 30 c.c. of benzene, 25 c.c. of water are added, and after vigorously shaking for fifteen seconds the aqueous layer is drawn off and measured. The increase in volume is due to the acetic acid present, and multiplied by 4 gives the percentage of acetic acid. Some small amount of acetic anhydride will dissolve in water and some of the dilute acetic acid will dissolve in the benzene. A table of corrections is necessary. In the following pairs of figures the first is the burette reading of increased volume multiplied by 4 and the second the corrected percentage: 93.5—100, 90—95.6, 85—89.6, 80—81.5, 75—75.8, 55—55.1, 50—50.1, 35—33.3, 25—21.7, 20—15.5, 11—0. CHEMICAL ABSTRACTS.

**Colour Test for Oxalic Acid.** LEWIS H. CHERNOFF (*J. Amer. Chem. Soc.*, 1920, **42**, 1784—1785).—A few crystals of resorcinol are dissolved in 5 c.c. of the solution by warming gently. The

liquid is cooled and an equal volume of concentrated sulphuric acid slowly poured in to form a layer. A blue ring is formed at the junction of the layers if oxalic acid is present. If the blue colour does not appear, the liquids are mixed by shaking, and, after cooling somewhat, another 5 c.c. of sulphuric acid added. If the colour still fails to appear, the liquid is warmed over a flame (not boiled), when an indigo-blue colour appears. If the mixture is boiled the colour becomes dark green.

J. R. P.

**Detection of Coumarin in Vanillin.** L. GERET (*Mitt. Lebensm. Hyg.*, 1920, **11**, 69—71).—Five % of coumarin in vanillin can be detected by the yellow turbidity produced by the addition of a 1% solution of iodine in 2% potassium iodide solution; the turbidity changes to lustrous, metallic, bluish-black crystals containing 46.47% of iodine and yielding 13.36% of ash.

CHEMICAL ABSTRACTS.

**Estimation of Aminoethyl Alcohol and of Choline appearing on the Hydrolysis of Phosphatides.** P. A. LEVENE and T. INGVALDSEN (*J. Biol. Chem.*, 1920, **43**, 355—378).—The method is a modification of that introduced by Thierfelder and Schulze (*A.*, 1916, **i**, 548). This method is employed in the original form up to the point where the free aminoethyl alcohol is extracted. This is accomplished by boiling the mixture of the hydrochlorides of the two bases and an excess of calcium oxide with dry acetone. The combined acetone extracts are acidified with hydrochloric acid, and evaporated in a vacuum. The residue is dissolved in water, evaporated to a syrup, and again treated with calcium hydroxide and acetone. The final acetone extracts are filtered, made acid with hydrochloric acid, and the acetone removed by vacuum evaporation.

The residue from the acetone extracts is treated with water and filtered from calcium hydroxide. Hydrochloric acid and the residual calcium are removed by silver oxide and carbon dioxide respectively. The choline is precipitated as picrate.

In an actual experiment on the separation of the bases from the ether-soluble, acetone-insoluble lipoids from egg, 77.5% of the amino-nitrogen was found present in the acetone extracts, whilst the yield of choline was 98.7% of the theory.

J. C. D.

**Separation and Estimation of Phenylalanine.** SHINTARO KODAMA (*J. Tokyo Chem. Soc.*, 1920, **41**, 479—495).—In the ester or the lime method glutamic acid, aspartic acid, and phenylalanine are collected in the same fraction. The author adds lime to the mixture of the products of hydrolysis of a protein, whereby basic calcium glutamate is precipitated. The calcium salts subsequently obtained by concentrating the filtrate are washed with water or lime-water, heated with 7 to 8 volumes of water, and treated with carbon dioxide, whereby calcium carbonate is precipitated. When this filtrate is concentrated, phenylalanine crystallises.

An approximate estimation of the phenylalanine in a mixture of the calcium salts of phenylalanine (Ca, 9.98; H<sub>2</sub>O, 8.91%), glutamic

acid (Ca, 16.80;  $H_2O$ , 22.56%), and aspartic acid (Ca, 16.51;  $H_2O$ , 29.63%) can be made if the percentage of calcium and of water of crystallisation is estimated. By suspending the mixture in hot water and treatment with carbon dioxide, calcium glutamate and aspartate lose one-half of their calcium, and are converted into easily soluble, normal calcium salts, whilst the calcium salt of phenylalanine loses the whole of its calcium, and is converted into the free acid. The difference between the amount of calcium in the precipitate and in the solution corresponds with the amount of calcium originally combined with phenylalanine.

Several methods of obtaining perfumes from phenylalanine are described.

CHEMICAL ABSTRACTS.

**Estimation of Taurine in Muscle.** Y. OKUDA and KEIICHI SANADA (*J. Coll. Agr. Imp. Univ. Tokyo*, 1919, 7, 77—80).—Sulphur is estimated in an aqueous extract of the muscle, after removal of all compounds of sulphur except taurine, for example, proteins, sulphates, and cystine (if necessary). The flesh (5 grams if fresh, 1 gram if dry) is ground and extracted first with cold water, then with warm water. The total extract is boiled with the addition of acetic acid; the coagulum is removed; the filtrate is neutralised, and is precipitated with basic lead acetate, an excess of that reagent being avoided. The precipitate is removed by filtration; the filtrate is treated with sulphuric acid to precipitate the excess of lead; excess of sulphuric acid is removed with baryta, and excess of baryta with ammonium carbonate. The final filtrate is used for the estimation of sulphur, which is converted into sulphate and weighed as barium sulphate. Multiplication of the weight of barium sulphate by the factor 0.5358 gives the weight of taurine. Cystine is usually absent from the extract; if it is present, the above technique is modified; after precipitation of the excess of lead, more sulphuric acid is added until its concentration reaches 5%; the cystine is then precipitated with phosphotungstic acid and removed by filtration after remaining for two or three days. Treatment with baryta and with ammonium carbonate and estimation of taurine sulphur are made as usual. The percentage of taurine in fresh flesh and, in parentheses, in dry flesh, was: shark, 0.13 (0.61); carp, 0.13 (0.61); ordinary flesh of bonito, 0.08 (0.30); "chiai" flesh of bonito, 0.42 (1.56); *Neptunus pelagicus*, 0.28 (1.37); *Palinurus vulgaris*, 0.17 (0.76); *Pinna japonica* (adductor muscle), 0.54 (2.38); *Avicula martensii* (mantle), 0.91 (5.20). All the samples of muscle (fish, mollusc, and crustacean) examined contained taurine; that compound was most abundant in molluscs, and less abundant in fish, although present in comparatively large amount in their "chiai" flesh.

CHEMICAL ABSTRACTS.

**Detection of Cyanic Acid.** R. FOSSE (*Compt. rend.*, 1920, 171, 635—637).—The cyanic acid may be detected directly as such or after its conversion into silver cyanate. In the first case a portion of the solution is heated for one hour with ammonium chloride, and the carbamide present in 2 c.c. of the solution thus

treated and in 2 c.c. of the untreated solution is estimated by means of xanthhydrol. An increase in the carbamide content of the solution by heating with ammonium chloride is evidence of the presence of cyanic acid. In the second case the silver cyanate is heated with ammonium chloride, and the resulting liquid tested for carbamide as above. Another portion of the silver cyanate is first heated with nitric acid and then with ammonium chloride, but in this case there is no formation of carbamide. W. G.

**Volumetric Estimation of Thiocyanate by Potassium Permanganate.** R. MEURICE (*Ann. Chim. anal.*, 1920, [ii], 2, 272—273).—Trustworthy results are obtained when the thiocyanate solution is acidified with sulphuric acid, treated with an excess of standardised potassium permanganate solution, and the excess of the latter then titrated with dilute hydrogen peroxide solution. The excess of permanganate added should be at least one-half of that required for the oxidation of the thiocyanate. Direct titration of thiocyanate in acid solution with permanganate yields low results. W. P. S.

**Detection of Hydrogen Cyanide.** JAMES MOIR (*J. S. African Assoc. Anal. Chem.*, 1920, 3, 16. Compare P., 1910, 26, 115).—Filter paper is moistened with a reagent consisting of *o*-tolidine 1 gram, copper acetate 1.5 grams, glacial acetic acid 0.5 gram, and water 100 c.c., and is then suspended in the atmosphere to be tested. A blue colour appears on the paper if the air contains as little as 1 part of hydrogen cyanide in 2 millions. W. P. S.

**Preparation of Phosphomolybdic Acid and its Application to the Colorimetric Estimation of Uric Acid.** P. PROSCHOWSKY (*Kongl. Vet. Landbohögskole Aarskrift*, 1918, 372—407; from *Chem. Zentr.*, 1920, iv, 315).—The author reviews the colorimetric methods which have been proposed for the estimation of uric acid in urine, and indicates a new procedure for the preparation of phosphomolybdic acid required in Höst's process; the latter has been examined in detail, and certain improvements are recommended. H. W.

**Nuclein Metabolism. IX. Detection and Estimation of Combined and Free Purines in Human Blood and Pus Serum.** S. I. THANNHAUSER and G. CZONICZER (*Zeitsch. physiol. Chem.*, 1920, 110, 307—320. Compare A., 1919, i, 228).—For the estimation of the free purines in blood the serum is diluted with water and precipitated with 1.55% uranium acetate. The filtrate is boiled with some sodium acetate and sodium hydrogen sulphite and precipitated with 10% copper sulphate. The precipitate is centrifuged, washed, and the nitrogen in it is determined by the micro-Kjeldahl method. From the value obtained, the free purine content is calculated. The figures of the uric acid content of serum obtained by the colorimetric method and by the above method agree fairly well, and it is therefore to be concluded that only very

small quantities of free purines other than uric acid are present in the blood. In order to estimate the combined purines (nucleotides) in the blood, the diluted serum is boiled, and precipitated with a 20% solution of sulphosalicylic acid in order to remove the proteins. The filtrate is concentrated and the purines are precipitated with copper sulphate as previously described, and the total purines are obtained from the nitrogen estimation, whilst the combined purines are calculated by difference. One hundred c.c. of normal human serum contain 2—3 mg. of nucleotide nitrogen and 1—1.5 mg. of free purine nitrogen.

S. S. Z.

**Colorimetric Estimation of Adrenaline.** WILBUR L. SCOVILLE (*J. Ind. Eng. Chem.*, 1920, **12**, 769—771).—A mixture of 20 c.c. of water, 5 c.c. of 1% potassium iodate solution, and 0.25 c.c. of *N*/1-hydrochloric acid is heated at 38°, and 0.5 c.c. of a 0.1% solution of the sample is added. A similar mixture is prepared, but using 0.5 c.c. of pure adrenaline solution. Both mixtures are kept at 38° for fifteen minutes, then cooled, and the colorations compared. If the coloration of the test solution differs by more than 25% from that of the standard, the estimation should be repeated, using more or less of the solution. The pure adrenaline solution is prepared by dissolving 0.5 gram of the substance in 0.5 c.c. of *N*/1-hydrochloric acid and diluting the solution to 50 c.c.; if the solution to be examined contains sodium hydrogen sulphite, 0.05 gram of the latter should be added to the standard solution.

W. P. S.

**Important Source of Error in the Examination of Urine for Albumin with Sulphosalicylic Acid.** GRETE LASCH and JOSEF REITSTOETTER (*Munch. med. Woch.*, 1920, **67**, 484—485; from *Chem. Zentr.*, 1920, iv, 30).—Schall's assumption (this vol., ii, 398) that sulphosalicylic acid forms a precipitate with calcium chloride which can be mistaken for a precipitation of albumin is untenable.

H. W.

**Detection of Slight Traces of Hæmoglobin in Urine.** J. PITICARIU (*Compt. rend. Soc. Biol.*, 1920, **83**, 605—607; from *Chem. Zentr.*, 1920, iv, 31).—Spectroscopic examination of perfectly fresh urines which contain traces of hæmoglobin and to which Ehrlich's reagent (dimethylaminobenzaldehyde + hydrochloric acid) has been added, shows the characteristic absorption bands of oxyhæmoglobin at dilutions at which this is otherwise not the case.

H. W.

**[Quantitative Comparison of] Vitamine Content.** WALTER H. EDDY and HELEN C. STEVENSON (*J. Biol. Chem.*, 1920, **43**, 295—309).—The methods proposed by Bachmann (*A.*, 1919, i, 613) and by Williams (*A.*, 1919, i, 463) have been used for quantitative studies on the vitamine-*B*. A new technique is described which eliminates some of the difficulties in the manipulation of these two tests. It is shown that this method may be utilised in estimating the vitamine content of food.

J. C. D.

## General and Physical Chemistry.

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**Atomic Refraction.** W. SWIENTOSLAWSKI (*J. Amer. Chem. Soc.*, 1920, **42**, 1945—1951).—A theoretical paper in which it is shown that the atomic refractions of carbon and hydrogen in hydrocarbons vary with the constitution of the hydrocarbon. The molecular refraction,  $M_D$ , of a hydrocarbon  $C_nH_m$  may be expressed by the equation  $M_D = nr_{CH_2} + (m - 2n)r_H + \Sigma\Delta r_C + \Sigma\Delta r_H$ , in which  $r_C$ ,  $r_H$  and  $r_{CH_2}$  are the refractivities of carbon, hydrogen, and the group  $CH_2$  respectively. The individual refractivities may be evaluated from this equation when  $\Sigma\Delta r = \Sigma\Delta r_C + \Sigma\Delta r_H$  is assumed equal to zero. Making use of the known molecular refractivities of eight hydrocarbons, the values  $r_C = 2.490$ ,  $r_H = 1.066$ , and  $r_{CH_2} = 4.622$  are obtained as mean values. These values differ in two cases from Eisenlohr's values,  $r_C = 2.418$ ,  $r_H = 1.100$ , and  $r_{CH_2} = 4.618$  (A., 1911, ii, 81). The value for  $CH_2$  is in agreement, whilst the other values differ by  $\pm 3\%$ . This divergence is explained by the fact that the value for  $M_D$  comes from two factors,  $M_D = nr_{CH_2} + \Sigma r_X$ , of which the former is large, and consequently small errors cannot affect  $M_D$  to a marked extent. In the case of alcohols, the value  $r_O = 1.494$ , which is 2.03% smaller than Eisenlohr's value; for ethers  $r_O = 1.663$ , whilst Eisenlohr's value is 1.643, or 1.2% less. It is stated that the calculation of average values for atomic refraction is insufficient for practical purposes, and the change of the value with constitution must be taken into account.

J. F. S.

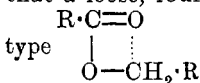
**The Molecular Refraction Coefficient, its Additivity and its Use for Determining Constitution.** FRITZ EISENLOHR and EDGAR WÖHLISCH (*Ber.*, 1920, **53**, [B], 1746—1766).—The molecular refraction calculated from the expression  $fn \cdot M/d$ , where  $fn = n^2 - 1/n^2 + 2$ , is not very sensitive to constitutive influences, and is unsuitable as a constant for determining the purity of a substance because, in the case of an impure substance, the refractive index and density may have a mutually compensating effect. It is claimed that the expression  $M \times n$ , termed the molecular refraction coefficient, is in many respects superior. This quantity has been calculated for a large number of organic compounds, using  $n_D^{20}$ , and has been found to be very sensitive to constitutive influences. In the paraffins, primary alcohols, aldehydes, ketones, acids and esters, the mean value of  $M \times n_D^{20}$  for  $CH_2$  is 20.56, for C, 25.55; H, -4.99. The values for oxygen are, in hydroxyl, 26.54; in ethers, 22.97; in aldehydes, 17.40; in ketones, 16.98. For the ethylenic double bond, -6.17 is found. It is to be noted that the influence of a double bond, whether between two carbon atoms or between carbon and oxygen, is negative, instead of positive as in the old molecular refraction. The probable error

in the above figures is 0.2 unit. The influence of a side-chain in the paraffin series varies with the position of the tertiary carbon atom. If the side-chain is attached to the second carbon atom, its effect is equal to -0.2 unit, but on the third or fourth carbon atom its sign is reversed, and it amounts to 0.45.

In cyclic, non-aromatic compounds, the effect of ring formation is more marked on the new molecular refraction-coefficient than on the old. The values found were -5.5, -4.9, -4.2, -3.4, -2.2, and -1.1 for the three- to eight-membered rings respectively. The entry of a side-chain into the six-ring system has a further lowering effect on the coefficient, and in the disubstituted compounds this negative effect is magnified, most in the para- and least in the ortho-compounds. The double bond in the polymethylenes has the same value as in the open-chain compounds, but in the substituted polymethylenes its influence depends on its position in relation to the side-chains.

In aromatic compounds, the allowance to be made is not equivalent to a six-membered ring with three double bonds, but the total effect is equal to -21.2 units. In contradistinction to the polymethylenes, the effect of substituents in the benzene series is positive. Certain numerical relationships appear to exist between the effects of substitution in the aromatic and polymethylene series respectively.

In the series of aliphatic acids and esters, certain optical abnormalities appear, which can be explained on the assumption that a loose, four-membered ring is present in the structure of the



E. H. R.

**Mass Spectra of Chemical Elements. II.** F. W. ASTON (*Phil. Mag.*, 1920, [vi], **40**, 628—634. Compare this vol., ii, 344).—The mass spectra of boron, fluorine, silicon, bromine, sulphur, arsenic, and phosphorus have been measured by the method previously described (*loc. cit.*). The results show that all seven elements obey the whole-number rule within the accuracy of the experiment. Of the elements examined, boron, silicon, and bromine are definitely complex; they are composed of two isotopes, in each case of the following relative masses: boron, 11, 10; silicon, 28, 29, (30); bromine, 79, 81; the masses are given in order of intensity, and the parenthesised number indicates a doubtful mass. In the case of bromine, two lines are obtained, corresponding with masses of 80 and 82; these correspond with hydrogen bromide from the two bromine isotopes; similarly, lines of two boron difluorides have been identified. Some anomalous fractional lines are mentioned and their possible origin discussed. J. F. S.

**Spectrum of Neon.** F. PASCHEN (*Ann. Physik*, 1920, [iv], **63**, 201—220. Compare this vol., ii, 69).—A theoretical paper in which the series occurring in the spectrum of neon are discussed. The neon spectrum is composed of ten sequences of the principal



series type and fourteen sequences of the subsidiary series type. The limits of the series which result by the combination of one set of sequences show a constant difference in wave-length of 782  $\text{cm.}^{-1}$  when compared with the combinations from the associated set, independent of the type of the series. This modification of the combination principle results when the limits of all series are calculated according to the Ritz formula. J. F. S.

**Comparison between the Spark Spectra of the Alkaline Earths and the Arc Spectra of the Alkalis.** ERWIN FUES (*Ann. Physik*, 1920, [iv], **63**, 1—27).—A theoretical paper in which arc spectra of the alkalis and the spark spectra of the alkaline earths are considered with the object of examining Sommerfeld and Kossel's second hypothesis, the displacement hypothesis, which states that an element in its spectral behaviour is displaced to that of the element occupying the preceding position in the periodic system when an electron is removed from its outer sheath by ionisation, that is, when it is brought into such a condition that it can emit its spark spectrum. The result of the theoretical consideration is to confirm the hypothesis. As an addendum to the paper, the doublet series are given in tables for magnesium, calcium, strontium, and barium, as well as the second subsidiary series of single lines for zinc, cadmium, and zinc, and the first subsidiary series of aluminium. J. F. S.

**Spark Spectra of some Elements in the Extreme Ultra-violet.** LÉON BLOCH and EUGÈNE BLOCH (*Compt. rend.*, 1920, **171**, 709—711).—A study of the spark spectra of antimony, arsenic, bismuth, and tin over the range  $\lambda=1850\text{--}1400$ .

In this region, antimony shows a number of sharp, intense lines. The spectrum of arsenic is composed of weak and often diffused rays. The two characteristic intense lines of arsenic in this region are  $\lambda=1805\cdot6$  and  $\lambda=1660\cdot8$ . Four new rays of tin,  $\lambda=1655\cdot3$ ,  $1656\cdot9$ ,  $1574\cdot6$ , and  $1570\cdot6$ , respectively, were obtained. The complete spectrum of bismuth between  $\lambda=1823$  and  $1390$  is given.

W. G.

**Effect of a Magnetic Field on the Intensity of Spectrum Lines.** H. P. WARAN (*Proc. Camb. Phil. Soc.*, 1920, **20**, 45—49). When a small portion of the capillary of a mercury discharge tube was subjected to a magnetic field of about 5000 *C.G.S.* units, the light was found to change in colour and intensity opposite the pole pieces. The tube originally gave the principal mercury lines 5790·66, 5769·6, 5460·7, 4916·0, and 4358·34, and the hydrogen lines 6563, 4861·5, and 4340·7; on applying the magnetic field, new lines at 5426, 5679, 5872, and 5889, as well as a very strong red line at 6152, appeared. Exhausting the tube still further and increasing the current to 5 milliamperes produced four faint lines at 6234, 6152, 6123, and 6072; the effect of the field on these lines is to increase the intensity of 6152 about five times, whilst the others, if they change at all, suffer a decrease in intensity. In

a hydrogen tube containing a trace of mercury, the helium lines are intensified, whilst hydrogen lines are practically unaffected, or even slightly reduced in intensity. In a neon tube containing a trace of hydrogen, the neon lines were considerably enhanced. The experiments indicate that in a mixture of monatomic and diatomic gases, the monatomic gases alone seem to be affected in a peculiar way, resulting in their spectrum lines alone being very considerably enhanced or brought out prominently, even when not visible at all previously. In the case of atmospheric air, the effect of the field is to bring out new lines which are not present without the field, and although one or two of these lines have the same wave-lengths as previously catalogued lines of oxygen or nitrogen, many of them have not been identified. J. F. S.

**Centres of Absorption of Coloured Solutions.** EMILIO ADINOLFI (*Atti R. Accad. Lincei*, 1920, [v], 29, ii, 38—41).—In view of the disadvantages attending the usual methods employed to ascertain the centres of the bands of absorption spectra, the author suggests the following procedure, which gives continuous absorption curves. The light, before impinging on the slit of the spectrograph, is passed through concentrations of the substance, diminishing regularly by diffusion. By means of a capillary funnel, the solution is passed to the bottom of a test-tube containing the solvent, the tube serving as a lens. The surface of separation between solvent and solution being arranged normally to the slit, the field of the spectrograph shows, prior to diffusion, a sharp demarcation between the part of the absorption spectra and that corresponding with the solvent alone. As diffusion begins, the centres of absorption become successively blunted in dependence on their intensity, and become distributed on a curve which is a function of the wave-length, the intensity of absorption, and the gradient of the concentration.

Photographic investigation shows that the absorption spectra of potassium and calcium permanganates exhibit eight centres of absorption, the third, with the wave-length 5255 Ångström units, having the greatest intensity. The two absorption spectra are identical within the limits of accuracy of the measurements made. The frequencies of the eight centres of the visible spectrum are connected by means of the relation  $\nu = \nu_m \pm 753n$ , where  $\nu_m$  represents the frequency of the maximum of the centres and  $n$  the whole numbers from  $-2$  to  $+5$ . T. H. P.

**Absorption of Light by Elements in the State of Vapour.** (SIR) J. J. DOBBIE and J. J. FOX (*Proc. Roy. Soc.*, 1920, [A], 98, 147—153).—The absorption of the elements selenium, tellurium, mercury, zinc, cadmium, phosphorus, arsenic, and antimony was determined. Reproductions of the spectra are given. In the case of selenium, there is an increase in the amount of absorption from  $510^\circ$  to about  $650^\circ$ , from which point it diminishes up to about  $850^\circ$ . These changes are accompanied by changes in colour of the

vapour. The spectrum of selenium shows many narrow and sharp absorption bands, and presents generally the same channelled character as the spectrum of sulphur (A., 1919, ii, 334). The maximum absorption corresponds with a vapour density indicating an average value of 3 atoms in the molecule. In the case of tellurium, the general absorption increases with rise of temperature up to about  $1250^{\circ}$ , after which it diminishes to about  $1350^{\circ}$ . The spectrum is channelled. At  $1250^{\circ}$ , the constitution of tellurium vapour would appear to be analogous to that of sulphur and selenium at  $650^{\circ}$ .

Zinc, cadmium, and mercury show a different behaviour. They are transparent to light as far as the spectrum of the Nernst filament extends, that is, to about 3100. Increase of temperature is not accompanied by the peculiar behaviour exhibited by sulphur, and (unlike the results with sulphur, selenium, and tellurium) increase in quantity of the element within the limits of the experiments has little influence on the spectrum.

Phosphorus, arsenic, and antimony show an increase of absorption with rise of temperature. It is concluded that this is closely associated with the breaking down of complex molecules. No absorption bands or indications of any kind of selective absorption were observed in the elements of this group.

The elements studied are divided into three groups: (1) Elements the vapours of which exercise no absorption or show only a few well-defined absorption bands; these are monatomic. (2) Elements in which the absorption gradually increases as the temperature is raised, but which show no other effect within the limits of temperature imposed by the method; these are tetratomic. (3) Elements in which the absorption increases with increase of temperature to a maximum, and afterwards diminishes. The sulphur and halogen elements belong to this group. The results are explained by the rearrangement of valencies accompanying the breaking down of complex molecules.

J. R. P.

**Influence of Dissociation on the Absorption of Potassium Permanganate.** EMILIO ADINOLFI (*Atti R. Accad. Lincei*, 1920, [v], 29, ii, 87—89).—The absorption spectrum of potassium permanganate is not influenced by the extent to which the salt is dissociated.

T. H. P.

**The Absorption Spectrum of Europium.** WILHELM PRANDTL (*Ber.*, 1920, 53, [B], 1726—1728).—The absorption spectrum of europium was examined with a solution containing 20 grams of oxide as nitrate in 100 c.c., through a depth of 10 cm. A weak but characteristic, sharp, narrow line was found at  $\lambda 579$ . This is probably identical with the line placed by Demarçay at  $\lambda 590$ . It was also found that Demarçay's band at  $\lambda 465$  is, in reality, a triplet, consisting of three strong, sharp lines at  $465\cdot6$ — $465\cdot3$ ,  $465\cdot0$ — $464\cdot7$ , and  $464\cdot6$ — $464\cdot3$ . In other respects, Demarçay's observations were confirmed.

E. H. R.

**Measurement of the Luminous Intensity Diffused by Argon. New Determination of Avogadro's Constant.**

J. CABANNES (*Compt. rend.*, 1920, 171, 852—854).—The author has determined the ratio,  $R$ , between the intensity diffused laterally by 1 c.c. of argon and the illumination of a normal plane by an incident luminous ray, the gas being illuminated by the radiation  $\lambda=4358$ . The value obtained for  $R$  with a sample of gas containing 91% of argon, 8.7% of nitrogen, and 0.3% of oxygen was  $(1.34 \pm 0.05) \times 10^{-8}/\text{cm}$ .

Further, the author has shown that the polarisation of the light diffused laterally by argon is almost complete, and applying the theory of Rayleigh, he finds for Avogadro's constant the value  $(6.90 \pm 0.25) \times 10^{23}$ .

W. G.

**Alkaline Earth-Oxygen Phosphorescent Substances.**

FERDINAND SCHMIDT (*Ann. Physik*, 1920, [iv], 63, 234—294).—A number of substances which become phosphorescent when subjected to light have been prepared from the oxides of calcium, strontium, and barium. These oxides were mixed, respectively, with a small quantity of one of the following substances: sodium chloride, sodium fluoride, sodium phosphate, calcium fluoride, magnesium fluoride, lithium phosphate, potassium hydrogen phosphate, and potassium borate, and thoroughly ground together; then a small measured quantity of a nitric acid solution of one of the following nitrates was added: bismuth, copper, manganese, or lead. The mixture was thoroughly mixed and heated to a red heat. These mixtures were excited by means of the light from a series of sparks between aluminium poles in water, and in this way the whole spectrum down to  $220\mu$  was obtained. The influence of different wave-lengths in exciting the phosphorescence was measured, as well as the position of the phosphorescent bands. From a comparison of the analogous oxygen, sulphur, and selenium phosphorescent substances, the following conclusions are drawn: (1) The positions of brightest phosphorescence after illumination and those of the bands are shifted to shorter wave-lengths in the oxygen compounds, and to longer wave-lengths in the selenium compounds in comparison with the sulphur compounds. This would point to the oxygen compounds having a smaller dielectric constant than the sulphur compounds, and the selenium compounds a larger dielectric constant. The bands of the oxygen compounds have a higher temperature position, and those of the selenium compounds a lower temperature position, than the sulphur bands.

J. F. S.

**The Existence of Intermediate States in the Phosphorescence of Calcium Sulphide deduced from the Study of its Conductivity.**

P. VAILLANT (*Compt. rend.*, 1920, 171, 713—714).—In continuation of previous work (A., 1912, ii, 419), much larger variations in the conductivity of calcium sulphide by exposure to diffused sunlight have been obtained. The conductivity increases with the time to a maximum, and then

decreases if the exposure is continued. The reverse occurs if the sulphide is then kept in obscurity at constant temperature, but the maximum reached in this case is much higher than during excitation. If during excitation the sulphide is removed to obscurity before the conductivity has attained its maximum, the latter continues to increase, but, however, a much lower maximum is much more rapidly reached.

W. G.

**Inorganic Luminescence Phenomena. I. [The Influence of] Crystalline Form, Flux, and Actual Fusion on the Phosphorescence of Zinc Sulphide.** ERICH TIEDE and ARTHUR SCHLEED (Ber., 1920, 53, [B], 1721—1725).—The flux may act in one of two ways in inducing the phosphorescence of such a substance as zinc sulphide; it may either favour the appearance of a particular phosphorescent, crystalline form, or it may intermolecularly increase the pressure or lower the melting point. In the case of zinc sulphide, the two possibilities were investigated by preparing the two crystalline modifications in as pure a form as possible, and by determining the effect of actually melting the zinc sulphide by the method already described (see this vol., ii, 757). Blende (sphalerite) was found to be non-phosphorescent in the pure state, but when prepared by heating amorphous zinc sulphide with potassium chloride in the proportion 2:1 at 800° for forty-eight hours, it was phosphorescent. Wurtzite, the hexagonal form, prepared by sublimation of zinc sulphide, taking the greatest precautions against contamination, was also non-phosphorescent. On the other hand, pure fused zinc sulphide was strongly phosphorescent. It follows that there is no connexion between phosphorescence and crystalline form in the case of zinc sulphide, whilst the effect of a flux can be reproduced by fusing the pure sulphide. Fused pure alkaline earth sulphides were also found to be phosphorescent.

E. H. R.

**Fluorescence, Dissociation, and Ionisation in Iodine Vapour.** K. T. COMPTON and H. D. SMYTH (Science, 1920, 51, 571—572).—(I) *Fluorescence and Ionisation*.—The fluorescence of gases and vapours is not generally accompanied by ionisation. Hence, the recent view has been that the primary effect of the exciting light is to cause one or more electrons to take positions or conditions of abnormally large potential energy, without being necessarily removed from the parent molecule. The authors have obtained experimental evidence of the correctness of this view from measurements of the minimum energy required to ionise a fluorescing molecule. The former requires 10 volts, the latter 7.5 volts, when excited by the green mercury line. The difference, 2.5 volts, corresponds with the quantum of energy of the frequency of the exciting light by the relation  $eV = h\nu$ . This offers direct evidence of the existence of molecules the electrons of which possess abnormal potential energy as a result of the exciting light. (II) *Dissociation and Ionisation*.—Two types of ionisation were discovered in iodine vapour, a very weak ionisation at 8.5 volts,

attributed to the ionisation of atoms present because of the hot filament, and a very intense ionisation at 10 volts, attributed to the ionisation of the molecules. The difference, 1.5 volts, corresponds exactly with  $V$  in the relation  $eV = W$ , where  $W$  is the heat of dissociation of iodine reckoned for a single molecule. Probably this method may be of value in determining heats of dissociation which are too high to be found by ordinary methods.

CHEMICAL ABSTRACTS.

### **X-Ray Fluorescence of certain Organic Compounds.**

H. S. NEWCOMER (*J. Amer. Chem. Soc.*, 1920, **42**, 1997—2007).—The author has studied the fluorescence induced in a large number of substances with the object of finding a substance which will convert X-rays into rays of wave-lengths which will be bactericidally active, that is, wave-lengths in the mid-ultraviolet. The fluorescence was judged as to its visibility by an eye accommodated to darkness, since it was found that in most cases the visible rays emitted were too feeble to blacken a photographic plate, and in those cases where a bright fluorescence was observed, the light was examined by a Hilger quartz spectrometer. Three inorganic salts, 308 organic compounds, apart from dyes, and 157 dyes were examined, some in solution and others in the pure condition. Of all these compounds, sodium bromide alone gives a fluorescence with a wave-length lying in the required region. Many of the organic compounds fluoresce brightly in the visible region of the spectrum, and a fair number of them give fluorescence which is capable of blackening a photographic plate. The fluorescence is not limited to any physical state, and the nature of the fluorescence excited in any material, both as to intensity and quality, is independent of the quality of the exciting X-rays and dependent on their energy alone. It is shown, incidentally, that air becomes slightly fluorescent under the experimental conditions. The X-ray tubes were fed by a current of about 15 milliamperes at 10,000 to 70,000 volts. J. F. S.

### **Specific Rotation of Optically Active Liquids in the Pure State and in Solution.**

W. DEUTSCHMANN (*Zeitsch. physikal. Chem.*, 1920, **95**, 385—406).—A theoretical paper in which it is shown that the specific rotation of active substances in solution may be calculated, when the assumption is made that the specific rotation of an active substance is a constant quantity at all concentrations and in all solvents. To make this calculation, it is necessary to accept the Dolezalek theory of concentrated solutions (A., 1909, ii, 22; 1910, ii, 184; 1913, ii, 481, 482; this vol., ii, 32). Apparent divergence between observed rotation values and the calculated values are explained by the formation of active compounds between the two components of the solution, or by the presence of associated molecules of the active substance. The equations put forward are applied to the experimental results of Scheuer (A., 1910, ii, 470) for solutions of diethyl diacetylitartrate

in ethylene dibromide, and it is shown that here both disturbing factors are present. For the sake of simplicity in calculation, it is assumed that the specific rotation of the double molecules is the same as that of the simple molecules, and the slight divergences between the calculated values and the observed values are taken to indicate that the above assumption is not entirely justified. The very marked dependence of the specific rotation of many substances on the temperature is due to a change in the degree of association with change of temperature, and also to the fact that the double molecules have a different specific rotation from the single molecules.

J. F. S.

**Photochemical Decomposition of Potassium Cobalt-oxalate and its Catalysis by Neutral Salts.** F. M. JAEGER and G. BERGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 84—94).—The decomposition of a solution of potassium cobalt-oxalate by light occurs as follows:  $2\text{Co}(\text{C}_2\text{O}_4)_3''' = 2\text{Co}(\text{C}_2\text{O}_4)_2'' + \text{C}_2\text{O}_4'' + 2\text{CO}_2$  and  $\text{Co}(\text{C}_2\text{O}_4)_2'' \rightleftharpoons \text{Co}'' + 2\text{C}_2\text{O}_4''$ . The reaction was studied under different conditions by Vránek (*Zeitsch. Elektrochem.*, 1917, **23**, 336). In the present experiments, a quartz mercury lamp was used as the source of light, and the reaction carried out in quartz vessels. The quantities of salt decomposed in identical intervals of time are approximately independent of the initial concentration, and are chiefly determined by the light energy absorbed. The reaction is therefore described as photocatalytic. Exact proportionality between the amount of decomposed substance and the time of exposure, with the same initial concentration, was not, however, found. This is attributed to the change of absorptive power of the solution. Exact experiments with the pure salt showed that the speed of reaction was relatively greater with the smaller than with the higher concentrations, and some disturbing influence appeared to be active. Addition of alcohol had no appreciable effect, but a strong influence on the speed of reaction was found to be exerted by neutral salts. Chlorides of potassium, sodium, lithium, magnesium and glucinum, and ferric chloride, were used. The curves exhibited a maximum of velocity with a certain concentration of each salt, and the action may pass over into a retardation. The maxima are situated at smaller concentrations as the valency of the cation is greater. Each ion has a specific effect in addition to that of its positive charge.

J. R. P

**New Theory of Photographic Phenomena.** A. DAUVILLIER (*Compt. rend.*, 1920, **171**, 717—719).—A further development of a new theory explanatory of photographic phenomena (compare this vol., ii, 654).

W. G.

**Ionisation and Production of Radiation by Electron Impacts in Helium, Investigated by a New Method.** K. T. COMPTON (*Phil. Mag.*, 1920, [vi], **40**, 553—568).—A method is described whereby ionisation and radiation may be distinguished

and the proportion of either estimated when both are present. The ionisation chamber is similar to that used by Franck and Hertz (A., 1913, ii, 174). A tungsten wire, 0.8 cm. long and 0.08 mm. diam., serves as a source of electrons; 3.5 mm. away from the tungsten wire is a platinum gauze. The electrons emitted are drawn toward the gauze by an accelerating potential difference,  $V_a$ ; some pass through the gauze, but then encounter a retarding potential difference,  $V_r$ , which is sufficiently greater than  $V_a$  to prevent any electrons reaching the electrode. This electrode is connected to a quadrant electrometer, and may gain a positive charge either from positive ions produced by ionisation of the gas or as a result of electrons emitted photoelectrically by ultra-violet radiation set up by impacts of the electrons. The electrode is 7 mm. distant from the gauze. The electrode consists of a ring of copper closed at one side by a thin platinum foil, and at the other by a platinum gauze. It is suspended on a platinum wire, and so arranged that either the gauze or foil may be presented to the radiation. Positive ions are received by the electrode equally well whichever side is presented to the radiation, but the two sides are differently affected by ultra-violet radiation, for when the gauze is presented, a large part of the radiation enters the electrode and does not result in a loss of electrons. Thus the ratio  $E_f/E_g$  of the electrometer deflexion with the foil or gauze exposed gives the proportion of the total effect which is due to both of the individual effects. Using this apparatus with helium, it is found that resonance radiation sets in at 20.2 volts and ionisation at 25.5 volts. Ionisation is observed between 20.2 and 25.5 volts in proportions increasing with the gas pressure and with the bombarding current density. Evidence is presented to show that this ionisation is a secondary effect, due to impacts against electrons which contain absorbed radiant energy of the resonance radiation from neighbouring atoms. This method of ionisation appears to be very important at high gas pressures. The present results are a complete confirmation of those of Horton and Davies (A., 1919, ii, 210).

J. F. S.

**Distribution of the Emission Intervals of the  $\alpha$ -Particles of Polonium.** (MME) MARIE CURIE (*J. Phys. Radium*, 1920, [vi], 1, 12—24).—The intervals between the emission of  $\alpha$ -particles by polonium have been studied in the case of 10,000 emissions from several preparations of the polonium used in connexion with the work on its spectrum and its change into lead. The emissions were recorded by an electrometer provided with a photographic arrangement for registering the deflexions caused by the individual  $\alpha$ -particles. The results had to be corrected for the slow decay of the activity of the polonium and for the failure of the electrometer to distinguish emissions separated by less than a certain minimum interval (doublets). The law derived from the theory of probability, that if  $\theta$  is the mean interval, the fraction of the total intervals of duration greater than  $\tau$  is  $e^{-\theta/\tau}$ , was completely



verified by the experiments. Curves in which the logarithm of the number of emissions, of interval greater than a given interval, are plotted against this interval, are straight lines, except for the smallest intervals (due to doublets, which can so be evaluated) and the longest, where the number is too few for the result to be accurate. By suitably combining all the results in one curve, a verification to an extreme degree of accuracy was obtained. The radioactive constant,  $\lambda$ , for polonium was redetermined, and found to be  $0.00496(\text{day})^{-1}$ , corresponding with a period of average life of 202 days, and of half change, 140 days, in agreement with the accepted value. F. S.

**Radioactive Analysis of the Thermal Springs of Bagnères-de-Luchon, Springs very Rich in Radium Emanation.** ADOLPHE LÉPAGE (*Compt. rend.*, 1920, 171, 731—733).—The waters from the various springs of Bagnères-de-Luchon were found to contain from 0.4 to 41.5 millimicrocuries of radium emanation per litre, and they thus form some of the most radioactive springs in the world. W. G.

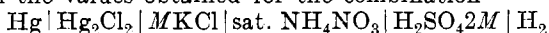
**The Variations of the Radioactivity of the Springs of Bagnoles-de-l'Orne and their Relation to the Rain.** P. LOISEL (*Compt. rend.*, 1920, 171, 858—860. Compare A., 1919, ii, 489).—The radium emanation content of the water of the springs at Bagnoles-de-l'Orne shows considerable variation, and this is correlated with the rainfall. The amount of radium emanation present rises and falls with increase or diminution in the rainfall, but the interval between maximum rainfall and maximum emanation content varies with the particular spring, and presumably depends on the nature of the strata through which the rain must percolate before reaching the spring. W. G.

**The Electrical Conductivity of Potassium, Sodium, and Barium Chlorides in Mixtures of Pyridine and Water.** JNANENDRA CHANDRA GHOSH (T., 1920, 117, 1390—1396).

**Hydrogen Overvoltage.** EDGAR NEWBERRY (*J. Amer. Chem. Soc.*, 1920, 42, 2007—2011. Compare MacInnes and Adler, A., 1919, ii, 131; MacInnes and Contieri, this vol., ii, 77).—A criticism of the above-mentioned papers. It is stated that the definition of overvoltage given is incorrect, and that the measurements recorded are not overvoltage measurements, but the excess potential necessary to overcome the transfer resistance, which in the experiments may have had values from 1000—100,000 ohms. The statements made about the dimensions of the overvoltage of platinum are incorrect. The hypothesis put forward is quite unable to account for the dependence of overvoltage on valency and many other phenomena, which are readily explained by the hydride or higher oxide hypothesis. The effect of pressure on overvoltage observed is due to changes in transfer resistance (see T., 1914, 105, 2428).

J. F. S.

**Stability of the Cobaltammines.** ARTHUR B. LAMB and ALFRED T. LARSON (*J. Amer. Chem. Soc.*, 1920, **42**, 2024—2046).—The oxidation potentials of six representative cobaltic amines have been measured in 3.265*M*-ammonium hydroxide solution. From these potentials, the concentration of the simple cobaltic ion in these solutions has been calculated, and the relative stability of the amines ascertained. The stability is very great compared with that of other metallic amines. The six amines, arranged in order of stability, are: aquo-pentammine cobalt chloride, diaquo-tetramminecobalt chloride, 1:2-dinitro-tetramminecobalt chloride, nitro-pentamminecobalt chloride, hexamminecobalt chloride, and 1:6-dinitrotetramminecobalt chloride. The stability constants of a number of metallic amines are calculated, and the following values obtained:  $\text{Ag}(\text{NH}_3)_2$ ,  $6.8 \times 10^{-8}$ ;  $\text{Cu}(\text{NH}_3)_2$ ,  $1.5 \times 10^{-9}$ ;  $\text{Cd}(\text{NH}_3)_4$ ,  $1.0 \times 10^{-7}$ ;  $\text{Zn}(\text{NH}_3)_2$ ,  $2.6 \times 10^{-10}$ ; and  $\text{Co}(\text{NH}_3)_6$ ,  $1.25 \times 10^{-5}$ . A series of other measurements have been made to obtain the data necessary in the above-named calculations; these include: (i) The measurement of the potential of the cobalt cobaltous electrode in cobalt chloride solutions at 25°, from which the normal potential  $\text{Co}/\text{Co}^{++}$  at 25° is found to be  $-0.237$  volt. (ii) The measurement of the potential of the cobalt cobaltous electrode in solutions of cobalt chloride in 6*M*-ammonium hydroxide, from which the formula of the cobaltous ammine ion is shown to be  $\text{Co}^{++}(\text{NH}_3)_6$ , and the equilibrium constant for its dissociation into ammonia and the simple cobaltous ion is shown to be  $1.25 \times 10^{-5}$ . (iii) The normal  $\text{Co}^{++}/\text{Co}^{+++}$  potential at 0° and 16° has been measured, and that at 25° extrapolated. The values obtained are: 0°, 1.775 volts; 16°, 1.779 volts; 25°, 1.817 volts. The temperature-coefficient of this value is  $+0.00169$  volt. (iv) The potential of the hydrogen electrode in 2*M*-sulphuric acid has been measured against the normal calomel electrode at 0° and 16°, when the values obtained for the combination



were: 0°,  $+0.2878$  volt, and 16°,  $0.2816$  volt. On the assumption that the normal hydrogen electrode has a zero temperature-coefficient, these give for the single potential  $\text{H}_2|2\text{MH}_2\text{SO}_4||$  the values 0°,  $+0.0012$  volt, and 16°,  $+0.0047$  volt, when Auerbach's values for the calomel electrode are employed (A., 1912, ii, 123).

J. F. S.

**Electrode Processes. Influence of Rise of Temperature and Depolarisers on the Form in which Nickel Separates.** HANS STÄGER (*Helv. Chim. Acta*, 1920, **3**, 584—613).—In order to throw further light on the connexion between polarisation and the form of metals deposited electrolytically, developed by Kohlschütter and Vuilleumier (A., 1919, ii, 9), the author has investigated (1) the formation or alteration of deposits of nickel under conditions effecting depression of the polarisation, and (2) the behaviour of these deposits when the development of the film of hydrogen, regarded as the true cause of the highly disperse metallic deposits, is suppressed by means of cathodic depolarisers.

As regards the course of the contraction of nickel deposits from different electrolytes, two types exist, the contraction in the one case gradually diminishing, whilst in the other it increases somewhat. The temperature at which the layer is formed influences the structure, and consequently the mechanical behaviour, of the deposit; since the development of a film of gas at the electrode must be rendered difficult by rise of temperature, the diminished dispersivity, and the resultant diminished capacity to sinter, which are observed may well be due to decrease in the deposit of hydrogen.

The experiments carried out on solutions containing depolarisers, such as hydrogen peroxide, nitrobenzene, potassium chlorate, and sodium cinnamate, show that the contraction of the nickel deposits is markedly diminished and their structure altered under these conditions, as should be the case if the discharged hydrogen is the ultimate cause of the effect. The results obtained when an alternating current is superposed to the direct current used for the electrolysis are also described.

T. H. P.

**Nature of the Spontaneous Alterations in Structure of Nickel Deposits.** V. KOHLSCHÜTTER (*Helv. Chim. Acta*, 1920, 3, 614—620).—The results obtained by Stäger (preceding abstract) and others are discussed.

T. H. P.

**An Electrolytic Current Intensification Effect, a New Electrolytic Displacement Effect and the Connexion between Electrolysis and the Emission of Electrons in a Vacuum.** D. REICHENSTEIN (*Zeitsch. physikal. Chem.*, 1920, 95, 457—507).—A theoretical paper in which it is shown that the conversion of an alternating current into a direct current by means of an electrolytic cell containing a passive metal cannot in any way be determined by the static characteristics in both directions, but only the dynamic characteristics are capable of giving information on such a transformation. The Schlömilch cell connected with a source of current is not only a detector, but, at the same time, a current intensifier. A scheme is described, useful in wireless telegraphy, whereby a strong intensification of current may be brought about electrolytically. This current intensification is an effect of the displacement principle. The action of the Schlömilch cell is explained on the basis of the new intensification effect. The potential difference electrode|vacuum may be calculated in exactly the same way as that existing between zinc and an aqueous solution of zinc ions. The electron emission in a vacuum can be expressed in the same way as electrolysis in chemical kinetic terms, whereby the divergences from Richardson's relationship and from Langmuir's spacial charge equation may be explained. These two relationships can only be regarded as limiting expressions.

J. F. S.

**Hydration of Electrolytic Ions.** RICHARD LORENZ (*Zeitsch. Elektrochem.*, 1920, 26, 424—431).—A theoretical paper in which,

making use of the author's work on space filling and the mobility of ions (this vol., ii, 481), it is shown that, by means of a modification of Stokes' law (Born, A., 1919, ii, 214; *Zeitsch. Physik*, 1920, 1, 220), the amount of hydration of electrolytic ions may be calculated. The space-filling number increases in proportion to the cube of the radius of the molecule, and, having determined the radius of the ion from the mobility by means of the modified Stokes law, the amount of hydration may be calculated. In the present paper, the hydration of ions is looked on as a sheath of water molecules round the ion, which is not necessarily made up of a simple number of molecules. The order in which the mobilities of the ions of the alkali metals occur is in quite the wrong direction for the atomic weights, but in view of the present arguments, the order of the mobilities is shown to be correct. Lithium possesses the smallest electrodynamic radius, and therefore moves most slowly, whilst caesium possesses the largest electrodynamic radius and moves fastest.

J. F. S.

**Disappearance of Gas in the Electric Discharge.** THE RESEARCH STAFF OF THE GENERAL ELECTRIC CO., LTD., LONDON (*Phil. Mag.*, 1920, [vi], 40, 585—611).—The present paper gives an account of an attempt to ascertain the cause of the disappearance of gas under an electric discharge at low pressure. Previous knowledge on the subject is briefly summarised. The parts played by absorption on the walls by chemical combination are unknown; it is also unknown what electrical conditions most favour the disappearance. Preliminary observations showed that the disappearance of gas was closely connected with the appearance of the glow in the vessel. In any given state of the discharge vessel, the glow appears sharply at a definite potential difference between the electrodes; this is termed the glow potential. The relationships existing between the glow potential and the thermionic emission, the pressure of the gas, the nature of the gas, and the form of the electrodes, respectively, have been examined. Small amounts of impurity change the glow potential very markedly, particularly in hydrogen. The general connexion between the appearance of the glow and the increase of ionisation is considered. The great importance of the glow potential for interpreting the rate of disappearance of gas is indicated. A number of experiments on the disappearance of carbon monoxide in the glow discharge are described. The results are discussed and explained by supposing that the glow causes a chemical change in the gas, which is reversible. The recognition of the reversibility appears necessary to explain the phenomena.

J. F. S.

**The Thermal Variation of the Coefficient of Magnetisation of Anhydrous Sulphates and the Theory of Magneton.** PH. THÉODORIDÈS (*Compt. rend.*, 1920, 171, 715—717).—If  $X$  is the specific coefficient of magnetisation in the case of each of the three anhydrous sulphates studied, namely, manganous, cobaltous, and ferric sulphates, the curve showing  $1/X$  as a func-

tion of the temperature consists of two parallel straight lines joined by a short, curved portion. In the case of two of the sulphates, this discontinuity is very close to the point at which the monohydrate loses its water, and it may therefore be due to a trace of impurity. In all these sulphates the molecular field is negative, and their virtual Curie point is below absolute zero. The results obtained conform with the theory of magneton. W. G.

**A Thermo-regulator.** J. FITCH KING (*J. Amer. Chem. Soc.*, 1920, **42**, 2058).—A device is described to prevent the contamination of the mercury surface in thermo-regulators which operate an electrical control of the heating arrangements. The contamination of the surface is due to oxidation when the small arc is produced at each break of the contact between the mercury and the wire contact. This can be avoided by replacing the air in the regulator by nitrogen. To do this, a small bulb is blown in the capillary tube at a short distance above the mercury surface, and in this bulb a globule of mercury is placed, so that a small volume of the tube is entirely cut off from the atmosphere. The wire contact passes through the globule, and can then make its contact in the usual way. The mercury globule rises and falls with the mercury surface below, but it never slips down and joins the lower mercury surface. The air space between the two mercury surfaces may be filled with nitrogen, but there is no need for this, as the small amount of oxygen is speedily used up, and then the surrounding gas is inert. J. F. S.

**Determination of the Thermal Conductivity of Water.** MAX JAKOB (*Ann. Physik*, 1920, [iv], **63**, 537—570).—A new method for the determination of the thermal conductivity of liquids is described. The thermal conductivity of water has been determined from  $7.4^{\circ}$  to  $72.6^{\circ}$ . A table of results is given, which may be represented by the formula  $\lambda = 0.4769(1 + 0.002984t)$ , in which the units are Cal.m.<sup>-1</sup>hour<sup>-1</sup>degree<sup>-1</sup>. In C.G.S. units (cal.cm.<sup>-1</sup>sec.<sup>-1</sup>degree<sup>-1</sup>), the formula is  $\lambda = 0.001325(1 + 0.002984t)$ .

The results are correct to 1%.

J. R. P.

**Radiation in Explosions of Hydrogen and Air.** W. T. DAVID (*Proc. Roy. Soc.*, 1920, [A], **63**, 183—198).—Mixtures of hydrogen and air were exploded in a closed vessel with black walls. The proportion of heat of combustion lost by radiation during explosion and cooling decreases greatly with the mixture strength. The total radiation emitted is a linear function of the maximum temperature developed. The proportion of heat lost by radiation up to the moment of maximum temperature varied between 0.5% (strongest mixture) and 1.4% (weakest mixture). The maximum rate of emission occurs approximately at the point of maximum temperature. Weak mixtures radiate more strongly in the initial stages of cooling than stronger mixtures when they have cooled to the same mean temperatures. The rate

of emission in the strongest mixture is approximately proportional to the fourth power of the absolute temperature. This does not hold in the initial stages of cooling of weak mixtures, but holds satisfactorily in the later stages. The  $2.8\mu$  emission band of steam ceases to be emitted when the temperature has fallen to about  $1000^\circ$  abs. The radiation contains wave-lengths greater and less than this. In experiments with silvered vessels, it was found that the intrinsic radiance increases with the size of the vessel, and the gases after explosion are very transparent throughout, cooling to radiation of the same kind as they emit.

The results are taken to indicate that the vibratory degrees of freedom of the steam molecules corresponding with radiation of  $2.8\mu$  share the heat energy of the molecules only above  $1000^\circ$  abs., and this may account for the rapid increase of specific heat in this region.

J. R. P.

**The Specific Heat of Saturated Vapours at Low Temperatures.** G. BRUHAT (*Compt. rend.*, 1920, 171, 712).—A reply to Ariès (this vol., ii, 585).

W. G.

**Aggregation at the Melting Point.** WILLIAM R. FIELDING (*Chem. News*, 1920, 120, 241—242, 255—256, 302—303; 121, 87—88, 150—153).—At the melting point, the molecules of each element are aggregated in a definite manner to form "melticules." The "melticular weights" of elements increase with the melting point. If the melting points are plotted against the melticular weights, all the elements lie on a single parabolic curve; if the melting points are close together, the curve is nearly a straight line. The rate of aggregation,  $R$ , is found by dividing the melticular weight by the molecular weight. If the quotient sp.ht./ $R$  is plotted against the melting point, the elements considered lie on a parabolic curve, but if m.pt.  $\times$  sp.ht. is plotted against  $R$ , the curve is nearly a straight line.

The specific heat is calculated by the formula

$$\text{m.pt.} \times \text{sp.ht.} / R = 4.15.$$

A table of melticular weights and values of  $R$  is given. All elements with abnormally low specific heats are polymerised. In each group of elements (with occasional exceptions), and very often in the same series, the specific heat falls with increase of atomic weight. The considerations are applied to compounds.

J. R. P.

**Clausius' Vaporisation Formula and a Comparison of the Vapour-pressure Curves of Two Substances.** FR. A. HENGLEIN (*Zeitsch. Elektrochem.*, 1920, 26, 431—436).—The Ramsay-Young and the Dühring rules have been deduced from the Clausius vaporisation formula, and thereby the physical significance of the constants occurring in these formulæ has been demonstrated. Dühring's rule is a special case of the general formula  $kT_1\theta_1/T_2\theta_2 = (T_1 - \theta_1)/(T_2 - \theta_2)$ , which holds even at high temperatures, and in which  $T_1$  and  $\theta_1$  are the boiling points of a substance

at two different pressures, and  $T_2$  and  $\theta_2$  the boiling points of another substance at the same two pressures. The constant  $k$  is approximately equal to the relationship between the molecular heat of vaporisation of the two substances. A formula is developed from the Clausius vaporisation formula which has the form  $\log T_1 = a \log T_2 + b$ . This formula holds exactly up to the critical point. In this formula,  $T_1$  and  $T_2$  are the temperatures at which both substances possess the same vapour pressure;  $a$  and  $b$  are constants. The constant  $a$  has a value between 0.8 and 1.5, and should it be exactly unity, the formula becomes the simplified Ramsay-Young formula. This equation is tested on a large number of substances in comparison with water. The agreement between the known experimental values and the calculated values is very good, so that it is practically possible to determine the vapour-pressure curve of a substance from that of water. The vapour-pressure regularities recently found by Herz (A., 1916, ii, 311) are explained. J. F. S.

**Finiteness of the Expression  $\int_0^T C/T \cdot dT$  in Wegscheider's Vapour-pressure Formula.** F. MAY (*Zeitsch. physikal. Chem.*, 1920, **95**, 434).—A theoretical paper in which it is shown that the integral mentioned in the title becomes at the lower limit an infinite function, and, further, the integral has no definite value, since  $\int_0^T a'/T \cdot dT = a' \lim_{\epsilon=0} \int_{0+\epsilon}^T = +\infty$ , a condition which Wegscheider (this vol., ii, 598) has not taken into account in his vapour-pressure formula. J. F. S.

**Finiteness of the Expression  $\int_0^T C/T \cdot dT$ .** RUDOLF WEGSCHEIDER (*Zeitsch. physikal. Chem.*, 1920, **95**, 435—437. Compare preceding abstract).—An answer to May's criticism of the author's vapour-pressure formula, in which the use of the integral in question is justified. J. F. S.

**Normal Vapour Pressures.** C. VON RECHENBERG (*J. pr. Chem.*, 1920, [iii], **101**, 112—122).—The present difficulty in making comparisons between the boiling points of substances determined under differing, diminished pressures leads the author to propose the adoption of a second standard pressure, which could be achieved by using a fraction of the physical atmosphere (760 mm.) or of the technical atmosphere (737 mm.), or a multiple of the absolute unit of pressure of the thermodynamic scale of the C.G.S. system. The latter course appears preferable, and a standard pressure equal to 15 mm. of mercury is suggested.

In the determination of boiling point under considerably reduced pressure, errors in the reading of the manometer are shown to be far more serious than those caused by incorrect reading of the thermometer.

On the basis of the Crafts-Young formula, the boiling points

of substances can be calculated to 15 mm., in accordance with the expression  $C = x(15 - p)(273 + t)$ , in which  $t$  is the approximately estimated boiling point under 15 mm. pressure,  $x$  is a coefficient depending on the nature of the substance, and  $C$  is the correction to be applied. In utilising the formula for the calculation of boiling point at atmospheric pressure, it is found adequate to divide substances into two classes, for one of which the mean value of  $x$  is 0.00010, and for the other 0.00012; for pressure below 25 mm., however, a further subdivision is necessary, and the following values of  $x$  are calculated from the recorded boiling points at 14—15 and 15—16 mm.; 0.004187 for hydrocarbons, ethers, oxides, thiocarbimides, mercaptans, sulphides, nitriles, and acid chlorides; 0.004009 for ketones; 0.003946 for esters, amines, and aldehydes; 0.003720 for phenols; 0.003574 for acids; 0.003458 for alcohols; 0.00301 for hydrazones; 0.002835 for quinones. The entrance of chlorine, bromine, or iodine atoms, or of the nitro-group, into a compound has less effect than isomerism on the coefficients. The calculations, both for 760 mm. and 15 mm., are only valid in the total absence of dissociation or other transformation. The calculation for 15 mm. is not designed for the correction of a boiling point determined at any reduced pressure to this particular value; if it is to be employed, the determination must be effected in such a manner that the reading of the manometer, which must be affixed to the boiling tube, only differs slightly from 15 mm.

H. W.

**Some Applications of the Method of Distillation in Steam.** JOSEPH REILLY and WILFRED J. HICKINBOTTOM (*Sci. Proc. Roy. Dubl. Soc.*, 1920, **16**, 131—142).—The suitability of the distillation method for determining molecular structure is discussed, but a consideration of the distillation constants of a number of compounds shows that, although the molecular structure may be inferred in certain cases, this method cannot be applied generally without the support of further evidence.

The distillation of solutions containing a volatile solute can be applied to detect changes in the state of molecular aggregation.

By reason of the fact that butter-fat contains appreciable amounts of butyric acid, whilst this acid does not occur in appreciable amounts in other fats of the type examined, butter-fat may be differentiated from these fats by the method of analysis of solutions by distillation. [See also *J. Soc. Chem. Ind.*, 1920, 804A.]

W. G.

**Calorimetric Procedure for Determining the Heats of Slow Reactions. II. Calorimetry of a Slow Reaction: Heat of Inversion of Sucrose by Acids.** FREDERICK BARRY (*J. Amer. Chem. Soc.*, 1920, **42**, 1911—1945. Compare this vol., ii, 533).—A method is described whereby the heat of inversion of sucrose by hydrochloric acid is measured with a precision largely determined by the characteristic errors of precise mercury thermometry. This reaction is exothermal, and involves a partial con-



current and endothermal heat of mixture, which, under favourable conditions, continues for nine hours. The adiabatic method, which alone is applicable in such determinations, is thus shown to be generally adequate for the precise calorimetric measurement, not only of swift reactions, but of any reaction which at ordinary temperatures requires less than a day for its completion. A way is thus indicated whereby chemical, kinetic, and total energy data may, in general, be directly correlated. The process itself is illustrative of such correlation. Incidentally, the procedure suggests a general and uniform method for the precise determination of adiabatic velocity-coefficients, and thus of the temperature-coefficients of velocity constants, by energy measurements alone. A number of modifications of the usual calorimetric practice are described. These are necessary for the measurement of the heats of slow reactions, but they are also generally applicable. Notice is taken of the probable source of error in mercury thermometry, due to the effect of radiation on encased thermometer threads. The following experimental data have been obtained: heat of inversion of sucrose by hydrochloric acid at  $20^{\circ}$ ,  $10.4 \pm 0.06$  gram cal. per gram; heat of solution of sucrose in water at  $20^{\circ}$ ,  $3.43 \pm 0.02$  gram cal. per gram for solutions up to about 4% sucrose concentration; heat of solution of sucrose in 1.64*N*-hydrochloric acid,  $4.23 \pm 0.05$  gram cal. per gram for solutions containing up to 4% sucrose; heat of solution of anhydrous  $\alpha$ -glucose in water at  $20^{\circ}$  and in 1.64*N*-hydrochloric acid at the same temperature,  $13.9 \pm 0.1$  gram cal. per gram for solutions containing up to 4% glucose.

J. F. S.

**The Principle of the Constant Sum of the Energy of Formation and its Partition between the Atomic Linkings in Aromatic Substances.** A. L. VON STEIGER (*Ber.*, 1920, 53, [B], 1766—1772).—In a previous paper (this vol., ii, 355), the energy of the C-C and C-H linkings in aromatic hydrocarbons was calculated, on the supposition that, in six-ring or condensed six-ring systems, the C-C and C-H linkings, respectively, are all equivalent. It is certain, however, that in such compounds all C-H linkings are not equivalent (in naphthalene, for example, the  $\alpha$ - and  $\beta$ -hydrogen atoms have different reactivities), but since the heat of combustion can be accurately calculated from constant  $x$  and  $y$  values for all C-H and C-C linkings, it follows that there must be some compensating effect at work. A principle of partition of the energy of the atomic linkings is worked out on the assumption that all the energy values may be different, and that the heat of decomposition of a  $>CH$  group is  $k_1 = y + x$ , and that of a carbon atom united to three others,  $k_2 = 3/2y$ , where  $x$  and  $y$  have the same significance as above. In other words, the sum of the energies of the linkings of each carbon atom is regarded as constant, instead of the energy of each C-C and C-H linking. In applying these assumptions to the consideration of hypothetical cases, it is assumed that when the energy of one linking of a carbon atom is increased, that of each of the two others is correspondingly

decreased. (Each aromatic carbon atom is regarded as tervalent, *loc. cit.*) It is shown that a change in the energy value of one such linking affects all the carbon linkings in the system, the effect diminishing as the distance from the disturbance becomes greater.

The energy value of the C-C linking in aromatic compounds is greater than in aliphatic compounds, and in the case of an aromatic-aliphatic linking, the value must lie between these two. For example, in toluene, the energy value of the side-chain C-C linking is higher than in an aliphatic compound, and the value for each C-H linking in the  $-\text{CH}_3$  group is correspondingly lowered, according to the above principle, with the result that the side-chain hydrogen atoms are more reactive in toluene than in ethane.

E. H. R.

**The Relation between the Physical Properties of some Organic Liquids.** W. HERZ (*Zeitsch. anorg. Chem.*, 1920, **112**, 278—282. Compare this vol., ii, 414).—In a former paper (this vol., ii, 285) it was shown that the quotient of the critical temperature and the critical pressure,  $T_k/p_k$ , divided by the sum of the valencies of the atoms in the molecule,  $z$ , is equal to a constant, 0.44, for a large number of non-associated compounds. Combining this with the expression  $T_k = \frac{1}{2}(1/k_{20} + 293)$ , where  $k_{20}$  is the coefficient of expansion at  $20^\circ$ , the critical pressure can be calculated from a knowledge of  $k_{20}$  and  $z$ . This has been done for a number of liquids of the aliphatic and aromatic series, with fair agreement between observed and calculated values of  $p_k$ . A relation is also deduced between molecular weight, critical density, and number of valencies, which is expressed by  $d_k = M/9.24z$ . This relation is checked against a large number of liquids of known critical density. The critical molecular volume assumes the simple form  $MV_c = 9.24z$ . From the relation  $L = 0.666p_k/d_k$ , where  $L$  is the heat of evaporation at the boiling point, combined with the above relationships, it follows that  $L$  can be calculated from a knowledge of  $k_{20}$ ,  $d_k$ , and  $z$ , or from  $k_{20}$  and the molecular weight by the equation  $L = 0.6993(1/k_{20} + 293)/M$ .

E. H. R.

**Comparative Method for Determining Vapour Densities.**

**II.** PHILIP BLACKMAN (*J. Physical Chem.*, 1920, **24**, 267—276).—A weighed amount of the substance is introduced into one limb of a U-tube over mercury. Air is present in both limbs. The apparatus is then heated in a bath until the substance is completely vaporised. Formulæ for calculation of the vapour density are given.

J. R. P.

**A Relation between the Volume and the Viscosity of some Organic Ions.** HOMER W. SMITH (*J. Physical Chem.*, 1920, **24**, 539—561).—The velocity of an organic ion is independent of the mass of the ion and of its configuration. It depends essentially on two factors, namely, the specific nature of the nucleus or polar group to which the ion owes its chemical properties, and the total volume of the ion. In any series of ions

having a common ionic nucleus, and no other (namely,  $-\text{COO}'$ ,  $-\text{NH}_3'$ ,  $-\text{NH}'$ , etc.), and apart from certain well-defined disturbing influences, the velocity is an inverse exponential function of the volume.

J. R. P.

**Fluidities and Specific Volumes of Mixtures of Ethyl Benzoate and Benzene.** EUGENE C. BINGHAM and LANDON A. SARVER (*J. Amer. Chem. Soc.*, 1920, **42**, 2011—2022).—The viscosity and density of mixtures of benzene and ethyl benzoate of a series of compositions have been measured at temperatures from  $5^\circ$  to  $75^\circ$ . From the experimental data, specific volume-temperature, fluidity-temperature, and fluidity-specific volume curves have been constructed. It has been stated that when inert liquids are mixed, the fluidity is a linear function of the volume composition. Benzene and ethyl benzoate neither undergo contraction nor is there any development of heat on mixing; they are therefore to be regarded as inert towards one another. At  $25^\circ$ , the fluidity-volume concentration curve is not linear, and the cube roots of the viscosities are a linear function of the molecular concentration. This indicates that benzene and ethyl benzoate must show quite perceptible concentration on mixing, which is proof of the aggregation demanded by the fluidity-volume concentration curve. Furthermore, the cube-root equation applies at only the one temperature used in the earlier work, but it does not apply at either higher or lower temperatures. This example is therefore not only not evidence against the fundamental hypothesis that fluidities are additive, but it furnishes strong evidence in its favour.

J. F. S.

**The Sorption of Copper Sulphide.** K. SCHERINGA (*Pharm. Weekblad*, 1920, **57**, 1294—1295. Compare A., 1918, ii, 409; 1919, ii, 367).—A curve given previously by the author for the carrying down of sodium chloride from solution by precipitated copper sulphide is found to hold only for very narrow limits; at different concentrations, very different quantities are carried down. The formation of a precipitate is probably preceded by the separation of structureless particles, surface tension being stronger than the directive force of crystal formation; these particles are able to adsorb other substances, a property which disappears as crystal formation sets in.

S. I. L.

**Sorption of Cellulose (Filter-paper) and Starch. Imbibition.** K. SCHERINGA (*Pharm. Weekblad*, 1920, **57**, 1289—1294).—The adsorptive power of filter paper is largely due to the distensible capillaries, which give it the character of a rather coarse, disperse medium. Since cellulose acts in water as a negative colloid, solutions of negative colloids, such as the metal sulphide sols, are stable towards it, whereas positive colloids, such as the metal oxide sols, are flocculated and suffer adsorption. The adsorption of neutral salts is slight, being relatively greater with more dilute solutions. The same is true for alkalis and alkaloids, but here the

adsorption is greater, and is completely inhibited by traces of acid. Since filter paper takes up ammonia and carbon dioxide from the air, all experiments were carried out with sheaves of paper dried at 120°.

In the case of starch, the behaviour is less simple, depending on the degree of hydration, the temperature employed, etc., but here also adsorption was relatively greater with more dilute solutions and largely inhibited by traces of acid. S. I. L.

**Deduction of the Dissociation Equilibrium from the Theory of Quanta and a Calculation of the Chemical Constants.** P. EHRENFEST and V. TRKAL (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 162—183).—A mathematical paper in which the conditions of equilibrium of a dissociating gas are deduced by statistical methods from the quantum theory. The relation between probability and entropy is discussed, and the ordinary calculations are extended by taking account of the grouping and motion of the atoms in the molecules. A vapour-pressure formula for very low temperatures is deduced.

On comparing the dissociation equation deduced with the corresponding thermodynamic equations, values are obtained for the chemical constants in the latter. J. R. P.

**Explanation of an Apparent Anomaly Outstanding in the Results of the Measurement of Dissociation Pressures.**

ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1920, **42**, 1951—1956).—The experimental dissociation pressures of Tamman (A., 1888, 403), Schottky (A., 1908, ii, 1016), and Partington (T., 1911, **99**, 466) have been outlined so as to elucidate an anomaly which is outstanding at the present time, namely, that the dissociation pressures of salt hydrates appear higher when measured by the gas current saturation method than when measured by the tensimetric method, and that tensimetric measurements yield readings which are greater at the beginning of the experiment than at the end. The explanations of this discrepancy put forward by Tamman (*loc. cit.*), Nernst (*Zeitsch. physikal. Chem.*, 1908, **64**, 425), Campbell (A., 1915, ii, 516), Partington (*loc. cit.*), and Brereton Baker (*Ann. Reports*, 1912, **8**, 34) are considered. A number of criticisms and suggestions in connexion with both methods are put forward. The dissociation pressure has been re-determined for copper sulphate pentahydrate by both methods, and the results of previous workers confirmed. It is shown that the results of the gas-current method are, as was to be expected to be, a little higher than those of the tensimetric method, and that the discrepancy observed is well within the experimental error of such measurements, consequently there ceases to be an anomaly. It is shown that the tensimetric results of Frowein (A., 1888, 337), often regarded as standards, should be accepted with caution.

J. F. S.

**Theoretical Investigations of the Condition of Dissociation. II. A. The Influence of Bivalent Ions. B. The Influence of Colloidal Condition.** L. MICHAELIS (*Biochem. Zeitsch.*, 1920, 106, 83—91).—A theoretical paper. S. S. Z.

**Spontaneous Velocity of Diffusion of Molten Lead.** J. GRÖN and G. VON HEVESY (*Ann. Physik*, 1920, [iv], 63, 85—92).—The spontaneous diffusion of molten lead has been determined by placing a layer of molten lead above a layer of a radioactive lead isotope (thorium-B) in a narrow, hard glass tube, and placing the tube in an upright position in a furnace of constant temperature for periods varying up to two days. After cooling, the lead was cut into sections, and the  $\alpha$ -ray activity measured in each piece. From the measurements, the quantity which had diffused to various heights was calculated. The results of seventeen experiments show, as a mean value, that 2.2 grams diffuse through an area of 1 sq. cm. per day at 343°. This value has been reduced to ordinary temperature and the viscosity of water, and the value 2.1 grams cm.<sup>2</sup>/per day obtained. This value is approximately three times as large as the velocity of diffusion of the lead ion in water, from which is deduced that the radius of the lead ion is at least three times as large as that of the lead molecule in molten lead, and in consequence the lead ion is regarded as being heavily hydrated. J. F. S.

**Osmotic Pressure Regarded as a Capillary Phenomenon.** H. HULSHOF (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, 23, 184—192).—A mathematical discussion of osmotic pressure on the basis of molecular attraction. J. R. P.

**Planck's Theory of Dilute Solutions.** P. BOEDKE (*Physikal. Zeitsch.*, 1920, 21, 551—552).—An extension of a former paper (this vol., ii, 229). Retention of terms of the second order in respect of concentrations in the expression for the potential is not sufficient to include known cases of equilibria. J. R. P.

**The Irregular Series of Flocculation.** H. R. KRUYT and (MME) H. G. VAN ARKEL-ADRIANI (*Rec. trav. chim.*, 1920, 39, 609—614).—From a study of the flocculation of neutral and alkaline gold sols by thorium nitrate and by colloidal thorium hydroxide, the authors conclude that, as a general rule, the irregular series are produced by the strong electro-capillary action of the ions, which discharge. It is only in the case of the intentional formation of an hydroxide sol, in alkaline medium, that the phenomenon of reciprocal flocculation occurs. W. G.

**The Relation between the Limit Value and the Concentration of Gold Sols.** H. R. KRUYT and A. E. VAN ARKEL (*Rec. trav. chim.*, 1920, 39, 615—617. Compare preceding abstract).—It has previously been shown for a sol of arsenious

sulphide that with the potassium ion the limit value increases with dilution of the sol, whilst with the barium ion it remains almost constant, and diminishes considerably with the aluminium ion. It is now shown that in the case of a gold sol the limit value increases either with a potassium, barium, or aluminium ion, and only diminishes slightly with the quadrivalent thorium ion.

W. G.

**The Critical Potential.** H. R. KRUYT (*Rec. trav. chim.*, 1920, **39**, 618—622).—A theoretical discussion of previous work (preceding abstracts), in which it is shown that for a given disperse substance the critical potential is only a constant within certain limits. It is necessary to take into account also the probability of adhesion.

W. G.

**Thermo-kinetic Explanation for the Reciprocal Attraction of Colloidal Particles. (A Possibility of Explaining Gravitation.)** ROBERT FRICKE (*Zeitsch. physikal. Chem.*, 1920, **95**, 441—456).—A theoretical paper in which the reciprocal attraction between colloidal particles in solution is shown to be due, in part, to kinetic actions, and not entirely to molecular attraction. The same conclusion is drawn for gas disperse systems, and a thermo-kinetic "shadow" hypothesis developed. This thermo-kinetic "shadow" hypothesis is further developed to a general energetic shadow hypothesis, which, on certain assumptions, is applied to other physical problems, particularly gravitation.

J. F. S.

**The Formation and Stability of Colloidal Solutions.** P. P. VON WEIMARN (*Ann. école mines de l'Oural*, 1919, **1**, 14—16).—Theories of the stability of colloidal solutions which are based entirely on the influence of ions, such as that of Malfitano (A., 1911, ii, 102), cannot be of general application, for, just as concentrated true solutions of a substance can be obtained in a solvent in which it is practically non-ionised, so can stable colloidal solutions of any substance be made in non-ionising solvents. Colloidal solutions of a substance in a dispersion medium in which it does not form a true solution cannot be prepared in more than very limited concentration unless a dispergator (peptising agent) be present.

CHEMICAL ABSTRACTS.

**The Fundamental Principles of Synthesis of Dispersoids in the Light of my Researches from 1906 to 1916.** P. P. VON WEIMARN (*Ann. école mines de l'Oural*, 1919, **1**, 1—5).—(A) General principles. (1) Any substance may be obtained in any degree of dispersion. (2) During solution of any substance in any solvent, the substance passes through the dispersoid state. Near a transition point the substance is in the dispersoid state. (B) Conditions for the dispersoid state irreversible with temperature. (I) Dispersoid solutions of low concentration result from reactions

producing the substance in a medium in which it is only slightly soluble, provided the reacting substances are very dilute. (II) Dispersoid solutions of higher concentration. (1) These coagulate at once in media which are practically completely indifferent to the disperse phase. (2) For the preparation of dispersoid solutions of higher concentration, conditions of dispergation (peptisation) (A., 1909, ii, 306; "Grundzüge der Dispersoidchemie," 1911, 76) and of dispersoid parasitism must obtain. (3) Homochemical compounds (barium sulphate forms homochemical compounds with all barium salts and all sulphates) exist for every substance and make it possible to realise conditions of dispergation and dispersoid parasitism. (III) Dispersoid precipitates. (1) These are obtained for any substance by carrying out the reaction forming it in a medium in which it is very slightly soluble. (2) A high degree of dispersion exists the longer the lower the solubility in the medium and the more indifferent to it. (3) The homo- and hetero-chemical cohesive forces exerted on the disperse phase by the dispersion medium and by substances in solution in it retard the union of the particles of dispersed phase, and hence the velocity of crystallisation. (C) Principles governing the dispersoid state reversible with temperature. (1) Any substance can be obtained by slow cooling of its solution as a highly dispersed gel or glass, which can be dissolved again on slowly warming. (2) By proper choice of dispersion medium, it can be made practically impossible to obtain the substance in the coarse state of dispersion. (3) The most important factors governing the ability to obtain the substance in reversible dispersoid state are: the solvation, "solventolysis," dispersoid parasitism, and the ability of the medium to solidify to a gel. (4) In systems in which the solubility decreases as the temperature increases, reversible dispersoids are obtained by processes the reverse of those used for systems in which the solubility increases with rising temperature.

## CHEMICAL ABSTRACTS

**Precipitation of Colloids.** HUMPHREY D. MURRAY (*Phil. Mag.*, 1920, [vi], **40**, 578—585).—A theoretical paper in which, from calculations based on Odén's data for colloidal sulphur and Freundlich's data for colloidal arsenious sulphide, it is shown that the minimal concentration of univalent cations required to precipitate a negatively charged colloid under similar conditions of concentration and temperature in a given time varies with the atomic number of the cation, and in general is given by an equation of the form  $C = K \cdot N^n$ , in which  $C$  is the concentration of the cation,  $N$  the atomic number of the cation,  $n$  a constant for the colloid at that particular concentration, and  $K$  a constant depending on the nature of the colloid and the anion. Taking the case of univalent cations with a common anion ( $\text{Cl}'$ ) and sulphur as the colloid,  $C_1 = 5.9N^{-1.64}$ ; potassium constitutes the only exception to this out of six cases examined. From a few examples, the equations  $C_2 = 1.46N^{-1.64}$  and  $C_3 = 0.33N^{-1.64}$  are obtained for

bivalent and tervalent cations respectively, where  $Cl'$  is the anion. In the case of anions with colloidal ferric hydroxide, the value  $C=0.00215N^{0.45}$  is obtained. In all cases, when  $\log C$  is plotted against  $\log N$ , straight-line curves are obtained. If the foregoing results are substantiated, it follows that Whetham's law requires modification, probably by comparing the precipitating power of only those ions for which the values of  $N^n$  are approximately equal.  
J. F. S.

**Gelatin as an Emulsifying Agent.** HARRY N. HOLMES and WILLIAM C. CHILD (*J. Amer. Chem. Soc.*, 1920, **42**, 2049—2056).—The formation of petroleum-water emulsions by the aid of gelatin has been studied. It is shown that the maximum lowering of the surface tension should be obtained. This is secured just as well by 0.3—0.4 gram of gelatin per 100 c.c. of water as by 1.0 gram. Acids, bases, and liquefying salts (sodium iodide, sodium chloride, and sodium nitrate) also lower it a little, whilst solidifying salts (sodium sulphate, tartrate, and citrate) raise it. Viscosity must not be increased more than a little beyond that of water. This means either that only a small amount of gelatin can be used or that the gelatin must be liquefied by the proper electrolytes. The latter method yields the better emulsion. An excess of acid, base, or liquefying salt should not be used. This probably means that the structure of the gelatin must not be entirely destroyed or that it must not be reduced nearly to molecular size. There is no convincing evidence that gelatin particles are withdrawn from the solution to form adhesion layers about the oil droplets. There is no evidence that, as the oil content is increased, the gelatin content must also be increased to produce as good an emulsion. This would certainly be the case were adhesion layers formed around the oil droplets. One gelatin content in a given volume of water can be selected which will make the best emulsion for all oil contents. The main factor in oil-water emulsification with the aid of gelatin is viscosity, not the maximum, but the most favourable, viscosity.  
J. F. S.

**Determination of the Number of Independent Constituents of a System of Substances.** LOUIS DUBREUIL (*Compt. rend.*, 1920, **171**, 720—721; *Bull. Soc. chim.*, 1920, [iv], **27**, 809—813).—A mathematical expression is deduced which gives the number of independent variables in functions of which the changes in the chemical composition of a system of compounds can be expressed.  
W. G.

**The System  $Na_2HPO_4$ - $NaCl$ - $H_2O$ .** TSURUJI OKAZAWA (*J. Tokyo Chem. Soc.*, 1920, **41**, 602—620).—Primarily with the view of finding convenient transition temperatures of some hydrate which might be used for calibrating scales between 35° and 42° for a clinical thermometer, the author studied the effect of sodium chloride on the transition temperature of the hydrate of disodium



phosphate. For the lower scale, the transition temperature  $35.4^{\circ}$  of pure  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O} + 5\text{H}_2\text{O}$  can be used. For the upper limit,  $39.3^{\circ}$  could be obtained if equal parts of the dodecahydrate and the heptahydrate of the phosphate and two-third parts of sodium chloride are mixed. More extended ranges of transition temperatures with various mixtures of the compounds and the nature of this system were studied in addition. The results obtained are given in three curves and two tables.

CHEMICAL ABSTRACTS.

**Theory of the Velocity of Chemical Reaction.** F. A. LINDEMANN (*Phil. Mag.*, 1920, [vi], **40**, 671—673).—A criticism of the hypothesis put forward by Lewis (T., 1918, **113**, 471). In this paper, Lewis shows that the velocity of a chemical reaction is determined by the energy density of radiation of a certain frequency. The present author points out that the radiation density may be profoundly modified by exposing the reaction to some external source of radiation, and, if Lewis's hypothesis is true, this should completely change the velocity of reaction, but no such phenomenon has been observed. Using Lewis's example for the inversion of sucrose by 0.9*N*-hydrochloric acid, it is shown that the reaction ought, on this hypothesis, to have a velocity  $10^{13}$  times as great in sunlight as in the dark. Yet the reaction actually proceeds at appreciably the same rate whether it is exposed to sunlight or not.

J. F. S.

**Formula for the Temperature Dependence of Velocity Constants in Gas Reactions.** J. TRESLING (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 143—148).—A mathematical paper in which the classical kinetic theory is applied, with special assumptions, to the derivation of formulæ for the dependence of reaction velocity on temperature.

J. R. P.

**The Velocity of Decomposition of High Explosives in a Vacuum.** I. ROBERT CROSBIE FARMER (T., 1920, **117**, 1432—1445).

**Rate of Chemical Action in the Crystalline State.** C. N. HINSHELWOOD and E. J. BOWEN (*Phil. Mag.*, 1920, [vi], **40**, 569—578).—The rate of decomposition of potassium permanganate at  $240^{\circ}$  and  $217^{\circ}$ , solid solutions of potassium permanganate and perchlorate at  $239^{\circ}$ , ammonium dichromate at  $219^{\circ}$ , potassium permanganate and manganese dioxide at  $220.5^{\circ}$ , and tetranitro-aniline at  $140^{\circ}$  and  $120^{\circ}$ , has been determined. The experiments were carried out with crystals of varying sizes, and the rate of reaction determined by the gas evolution. The change appears to be confined to those molecules in the neighbourhood of the surface, and in the region where a progressive disintegration of the crystal structure takes place the change is strongly accelerated. Solution in another solid causes a reduction in the rate of reaction. The results show that the molecules in the interior are under some kind of restraint; this may be connected with the fact

that in the interior the molecules are bound by valency forces on all sides, or it may be referred to the internal pressure.

J. F. S.

**Ideal Catalysis and the Theory of Dislocation.** J. BÖESEKEN (*Rec. trav. chim.*, 1920, **39**, 623—639).—A more detailed account of work already published (compare A., 1914, ii, 554, 847).  
W. G.

**Promoter Action in Catalysis.** ROBERT NORTON PEASE and HUGH STOTT TAYLOR (*J. Physical Chem.*, 1920, **24**, 241—265).—Promoter action in catalysis is understood as including all those cases in which a mixture of two or more substances is capable of producing a greater catalytic effect than can be accounted for on the supposition that each acts independently and in proportion to the amount present. An example is furnished by the use of iron-molybdenum in the synthesis of ammonia. Iron and molybdenum are both catalysts for the reaction, but a mixture of equal parts of the two is much superior as a catalyst to either alone. A distinction is made between this type of activation (co-activation) and cases (activation) in which a relatively inert substance increases the activity of a catalyst. Neutral salt action is an example of the second type. Examples of promoter action in heterogeneous and homogeneous catalysis and enzyme action are given.

J. R. P.

**The Constitution and Structure of the Chemical Elements.** HAWKSWORTH COLLINS (*Chem. News*, 1920, **121**, 219—222).—A continuation of a previous paper (this vol., ii, 680).

J. R. P.

**Constitution and Structure of the Radioactive Elements.** HAWKSWORTH COLLINS (*Chem. News*, 1920, **121**, 243—244).—The reasoning applied in previous papers (this vol., ii, 26, 680) is extended to radioactive elements. It is concluded that the characteristic constituent of these is a portion represented by hexadic titanium. This is shown to explain the emission of  $\beta$ -particles from the elements.

J. R. P.

**Atomic Structure and Chemical Properties.** EMIL KOHLWEILER (*Physikal. Zeitsch.*, 1920, **21**, 543—549).—In opposition to the prevailing views on the matter, the author considers that the chemical properties of an element are intimately connected with the constitution of the atomic nucleus. The constituents of nuclei are the helium nucleus, the hydrogen nucleus, and the electron. After the building up of a central nucleus, composed of a helium nucleus, or two hydrogen nuclei, for elements of even maximum valency, the uncompensated positive charges of the helium nuclei combine to groups of eight units. The residual, ungrouped charges, varying from 0 for the inactive gases, through 8 for the transitional elements, to 14 for the halogens, then deter-

mine the chemical characters of the element. The larger or smaller number of groups of 8 positive charges corresponds with analogous elements, whilst an equal excess or deficit of positive and negative units gives rise to isotopes. The theory enables many phenomena of valency, electrochemical character, etc. (A., 1918, ii, 304), to be explained. The action of the outer electrons may mask that of the nucleus, but the assumption that the latter is of no account in determining the chemical properties is none the less incorrect. Radioactive changes are quoted as examples of changes of chemical character due to alterations of the nucleus. The impossibility of changing the chemical character of an element is compared with the independence of radioactive properties on external conditions. Changes of valency, which are readily brought about, are conditioned by the external system. The views of Kossel (A., 1916, ii, 243) are adversely criticised. J. R. P.

**Stability of Atoms as Related to the Positive and Negative Electrons in their Nuclei, and the Hydrogen, Helium, H<sub>3</sub>, H<sub>2</sub> Theory of Atomic Structure.** WILLIAM D. HARKINS (*J. Amer. Chem. Soc.*, 1920, **42**, 1956—1997. Compare A., 1915, ii, 543, 544, 814; 1916, ii, 241; 1917, ii, 303; 1918, ii, 89; this vol., ii, 479, 541).—A theoretical paper in which the theory put forward in previous papers is extended. The negative electrons in the nuclei of atoms are largely associated in pairs, either as "binding" or "cementing" electrons. Pairs of binding electrons serve to bind together a number of positive electrons into a primary group or particle. The most abundant of these is the  $\alpha$ -particle, consisting of 2 negative and 4 positive electrons, and having a net positive charge of 2. Its formula is  $(\eta_4 + \beta_2)^{++}$ , where  $\eta^+$  is the positive and  $\beta^-$  the negative electron. The  $\alpha$ -particle makes up about 90% of all known material in meteorites. A second, less abundant, group is the  $(\eta_2 + \beta_2)^0$ , or  $\mu$ -group, which has a zero net charge, and makes up more than half of the rest of known material. Thus nearly all of the material, which consists of complex nuclei, exists in the form of groups made up of pairs of negative binding electrons, together with an even number of positive electrons. Isotopes of higher atomic weight differ from those of lower atomic weight by the presence of a single  $\mu$ -group, or of one or two "helio"-groups, or of both a helio- and a  $\mu$ -group. A helio-group consists of an  $\alpha$ -particle with 2 negative electrons, which cement it to the nucleus of the atom. Atoms of odd net nuclear charge are relatively rare; they consist mostly of  $\alpha$ -particles, but the odd value of the net charge is caused by the presence of one odd-numbered  $\nu$ -group,  $(\eta_3 + \beta_2)^+$ , in the nucleus of each atom of odd atomic number. Of the light atoms, only glucinum and nitrogen contain an odd number of negative nuclear electrons, and these elements are not abundant. Even among the radioactive nuclei there are only a few which contain an odd number of negative electrons, and they are very unstable. The  $\alpha$ -particle is assumed to be electrically negative in most of its

exterior, but to have a net positive charge of 2. Such particles repel one another at ordinary distances, and only attract when brought extremely close together in such a way that electrical couples are able to produce an attraction greater than the repulsion of the net charge. Neither a single positive nor a single negative electron can attach itself to such a particle, nor will two such particles unite, but three to eight, and also ten, but not more than ten,  $\alpha$ -particles unite to form a complex nucleus, in which the mass is twice the charge and the ratio of negative to positive electrons,  $N/P$ , is 0.5. Eleven positively charged  $\alpha$ -particles will not alone unite to form a complex nucleus, since the positive charge, 22, is too large for the attractive action of the particles to overcome the repulsive effect of the charge. More positive  $\alpha$ -particles will add on if, at the same time, the ratio  $N/P$  is increased. The ratio is increased by the addition of a heliogroup, which increases the ratio  $N/P$  by a sudden jump from 0.5 to 0.55. The increased ratio makes it possible for an extra positive  $\alpha$ -particle to attach itself, so two  $\alpha$ -particles are added in one step and two cementing electrons in addition. Thus the cementing electrons keep the nucleus stable as its self-repulsion increases. The atomic weight thus increases by 8 instead of the normal 4 units. More  $\alpha$ -particles then add on, decreasing the  $N/P$  ratio until the positive repulsion becomes so high that a second pair of cementing electrons adds on, and again the atomic weight increases with abnormal rapidity. It is shown that four series of atoms are known: the helium-thorium series, the meta-neon-uranium series, the lithium cobalt series, and the meta-chlorine series. The relationships of these series with the periodic system are discussed. The atomic weights of all pure series of atoms are very close to whole numbers when calculated on the  $O=16$  basis. Tables are given of the total positive charge, total negative charge,  $\alpha$ -cementing electrons, excess charge, and electron contents of the nuclei of all known atoms. When the net positive charge on the nucleus of an atom becomes greater than 28, the resultant self-repulsion becomes so great that relatively few atoms of this class can be formed. Such atoms are relatively rare, and do not make up more than 1/1000 of the material of the earth and meteorites, although they constitute more than two-thirds of the elements and more than three-quarters of the atomic species. In all common atoms, the ratio  $N/P$  is 0.5, or only very slightly above this value. The atoms become rare as soon as the cementing electron content rises above 2, and no number of cementing electrons is able to stabilise a nucleus with a positive charge greater than 28. Nuclei which contain an odd number of positive electrons are rare, and those containing an odd number of negative electrons rarer still. That is, atoms with an odd nuclear charge are rare, and when they do exist they are due to an odd number of positive electrons. Nickel is undoubtedly a mixture of isotopes; it has a low mean negative electron content, and therefore has a low atomic weight for its position in the periodic system. Nitrogen and scandium are not

members of any of the series mentioned above. Nickel, potassium, calcium, and iodine have abnormally low nuclear contents of negative electrons, whilst argon, tellurium, barium, and selenium have high contents. Most of these elements lie near the positions of atomic weight reversal in the periodic system. There are 92 elements in the limited sense of the term, but about 300 different species of atoms. The term element is now used to denote all atoms in the nuclei of which ( $P-N$ ) has the same value. All elements from Ge (atomic number, 32) to Au (97) are mixtures of isotopes.

The atomic weights of the light elements are mostly whole numbers on the oxygen basis, and in the case of even atomic weights are divisible by 4, which indicates that isotopes do not occur in these elements to a large extent; exceptions are to be found in neon, chlorine, magnesium, silicon, and probably aluminium. In other cases, from atomic number 28 to 80, the whole number atomic weights correspond with the law of chance. The atomic weights of lithium and boron indicate the existence of lighter isotopes, and the hypothesis indicates that the ratio  $N/P$  should be 0.5, so the atomic weight of the lighter lithium, which is probably present to the extent of 6% in lithium, is 6, whilst that of boron is 10; an isotope of iron, 52, calcium, 44, and several of nickel, 56, 60, and 58, are all indicated. Atoms of zero atomic number may exist with masses 4, 3, 2, and 1, and possibly other values. These would contain no non-nuclear electrons, and would have no chemical and almost none of the ordinary physical properties, apart from mass.

The whole number relationship of the atomic weights when  $O=16$  may be stated in the form that in all known complex nuclei the positive electron has the weight  $1.000 \pm 0.001$ , whilst the free positive electron has the mass 1.007. This might be stated more accurately by giving the weight of the average electron pair, as  $1.000 \pm 0.001$  in any complex atom, but as 1.0077 in hydrogen itself, where the positive electron is free and not bound. The constancy in the packing effect may be a characteristic of the positive and negative electrons themselves.

J. F. S.

### **The Possible Existence of Binding Rings in Diamond.**

N. H. KOLKMEIJER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 120—128).—A mathematical paper. The author agrees with Debye and Scherrer (*A.*, 1919, ii, 20) in rejecting the binding rings of two electrons between the carbon ions in the diamond as a satisfactory explanation of the forces of valency.

J. R. P.

**Considerations on Certain Numerical Relations Presented by Atomic Weights.** EDMOND JANDRIER (*Mon. Sci.*, 1920, [vi], **10**, 169—172, 194—198).—The alkali metals have atomic weights given by the formula  $m7 + n16$  ( $n=0$  for Li); those of the alkaline earths have atomic weights given by  $79 + m15 + n16$ . Thallium is considered an alkali metal, and bismuth a metal of the alkaline earths. The metals of the third

group have atomic weights of the form  $11 + m16 + n17$ , with the exception of gallium. Lead also follows this formula, and is considered as belonging to a branch group. Similar relations are deduced for other elements, and structural formulæ for atoms are given.

J. R. P.

**Binuclear Theory of Atoms and the Periodic System.** O. HINSBERG (*J. pr. Chem.*, 1920, [ii], 101, 97—111).—A further extension of the author's theories (compare A., 1916, i, 725; 1917, ii, 173, 461; 1918, ii, 106; 1919, ii, 505). It is assumed that there are three different arrangements of electrons within the atom: (i) nuclear electrons, which, as deduced by Fajans and Soddy from the occurrence of isotopic elements, have no direct influence on the chemical and physical properties of elements (with the exception of radioactive properties), but only an indirect effect in so far as they neutralise the positive charges of a nucleus, and so influence the number of free positive charges on the atom; (ii) valency electrons, which cause the formation of molecules by a process of neutralisation with the nuclei of other atoms; when situated at the exterior of the atoms, they are causative of the optical and chemical properties of the latter; (iii) ring electrons, which are placed between two nuclei, and, according to the simplest assumption, vibrate in a plane perpendicular to the axis of the two nuclei. A distinction is drawn between reversible ring electrons (which may pass into valency electrons by partial or complete obliteration of the internal ring, whereby they proceed to the neighbourhood of the nucleus) and irreversible ring electrons (in which this process is impossible). They play no part in the valency question. The inactivation of a valency electron is caused by its transition to an irreversible ring position. They are only of secondary importance for the physical, and particularly for the chemical, properties of the atoms. The author illustrates his arguments by a number of examples chosen from the group of the rare earths and from the formation of simple chemical compounds. He is thus led to the conception of intra-atomic union. The formation of molecules is a continuation of the formation of atoms; in other words, the production of molecules is due to the neutralisation of nuclei which have been unable to complete this process within the atom. This is impossible in those cases, instanced by the rare gases, in which intra-atomic neutralisation is quantitative. The molecules are atoms of a higher order.

The investigation includes the consideration of the chemical properties as well as the atomic volume and boiling point of the elements. It is less exact and certain than the methods of atomic physics, but provides material for this branch of the work, which is the more valuable since considerable difficulties are encountered in the mathematical treatment of the electronic theory of atoms based solely on physical data. In this connexion, a protest is made against the recent dictum of Stock, that the investigation of atomic structure is the province of the physicist alone.

H. W.

**A New Periodic Relation between the Atomic Weights of the Chemical Elements. III. Resonance Theory of Chemical Compounds. IV. The Connexion between Rests and Magnetic Susceptibility of Atoms.** KARL FEHRLE

(*Physikal. Zeitsch.* 1920, **21**, 552—555; see this vol., ii, 303).—

1. The frequencies of the inactive gases calculated by the author's formula are in the ratios of simple fractions. The resonance cannot be improved by combination with other atoms, which explains the inactive character of the elements. Relations between the frequencies of atoms and molecules are discussed. 2. The form of the curve of atomic diamagnetic susceptibility is that of the differences between the experimental and ideal atomic weights ("rests"). A theory of the magnetic properties on the basis of the resonance theory is given.

J. R. P.

**Which Elements Form Volatile Hydrides?** FRITZ PANETH

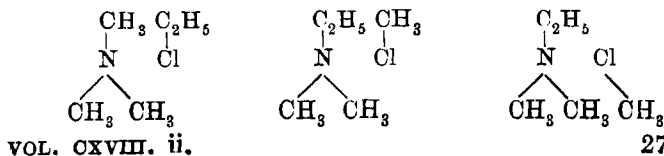
(*Ber.*, 1920, **53**, [B], 1710—1717).—The place in the periodic system of those elements which are known to form volatile hydrides is discussed. The discovery of volatile hydrides of tin, lead, bismuth, and polonium (this vol., ii, 41, 758) makes it possible to draw a sharp line between those elements which do, and those which do not, form volatile hydrides. When Staigmüller's form of the periodic table is considered (*A.*, 1902, ii, 129), in which the elements are divided into eighteen groups (the number of elements in a complete long period), it is seen that all the elements in the last four groups, including the above four elements, form volatile hydrides. Only one element not appearing in this portion of the table, boron, is known to form a volatile hydride. In other words, the four elements immediately preceding each noble gas, and boron, are the only ones which form volatile hydrides. The strange association of silicon, tin, and lead in the table is justified by the fact that they all form volatile hydrides, apart from their metallic or non-metallic character. The bearing of Kossel's views (this vol., ii, 681) on the volatility of the hydrides, considered from the space-lattice point of view, is discussed.

E. H. R.

**Subsidiary Valencies and Molecular Compounds.**

EDMUND NEUSSER (*Zeitsch. physikal. Chem.*, 1920, **95**, 439—440).

—A theoretical paper in which it is shown that the hypothesis as to the nature of subsidiary valencies and the formation of molecular compounds put forward by Hocheder (this vol., ii, 612) leads to consequences which are not in accord with known facts. Thus, according to the hypothesis, three isomerides should be formed when ethyl chloride is added to trimethylamine. These compounds would be formulated respectively:



The sulphato- and oxalato-pentammine cobaltic salts, which are known not to be ionised in solution, must, according to Hocheder's hypothesis, be dissociated to 50% with respect to the sulphate or oxalate group. Other difficulties are quoted in connexion with hexammine platinum chloride and copper thiocarbamide chloride.

J. F. S.

**Isomerism, Tautomerism, and Pseudomerism of Organic Compounds and their Relations.** INGO W. D. HACKH (*Chem. News*, 1920, **121**, 85—87).—Isomerism, tautomerism, metamerism, desmotropism, and pseudomerism are caused by six factors: *N*, the number of atoms in the molecule; *K*, the kind of atom; *P*, the position or arrangement of the atoms; *T*, the chemical type of the compound; *V*, the valency of the principal atom; *L*, the linking between the atoms. The following table gives a classification of the various types of isomerism on this basis:

Organic molecules or radicles show:

	<i>K</i> .	<i>N</i> .	<i>P</i> .	<i>T</i> .	<i>V</i> .	<i>L</i> .	
Isology when .....	<i>d</i>	<i>s</i>	—	—	—	—	(structure the same)
Homology when .....	<i>s</i>	<i>d</i>	—	—	—	—	( " " " )
Polymerism when .....	<i>s</i>	<i>d</i>	—	—	—	—	(percentage the same)
Structure isomerism when	<i>s</i>	<i>s</i>	<i>d</i>	—	—	—	(two-dimensional)
<i>cis-trans</i> -Isomerism when.	<i>s</i>	<i>s</i>	<i>d</i>	—	—	—	(three-dim., inactive)
Stereoisomerism when ...	<i>s</i>	<i>s</i>	<i>d</i>	—	—	—	(three-dim., active)
Metamerism when .....	<i>s</i>	<i>s</i>	<i>d</i>	<i>d</i>	<i>s</i>	<i>s</i>	
Desmotropism when .....	<i>s</i>	<i>s</i>	<i>s</i>	<i>d</i>	<i>s</i>	<i>d</i>	
Tautomerism when.....	<i>s</i>	<i>s</i>	<i>d</i>	<i>d</i>	<i>s</i>	<i>d</i>	
Pseudomerism when .....	<i>s</i>	<i>s</i>	—	—	<i>d</i>	—	

where *s*=same, *d*=different, and —=same or different.

Special symbols are given to express these relationships.

J. R. P.

**Method of Measuring the Rate of Flow of Gases.** JOSEPH ERLICH (*Ann. Chim. anal.*, 1920, [ii], **2**, 289—297).—The apparatus described is of the type in which the upper ends of a U-shaped manometer are connected by a capillary. The gas to be measured enters by a side-tube on one limb of the manometer, passes through the capillary, and escapes through a side-tube on the other limb, the pressure caused by the passage of the gas through the capillary being registered by the change in level of the liquid in the manometer.

W. P. S.



## Inorganic Chemistry.

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**Laboratory Apparatus for Preparing Electrolytic Hydrogen.** WILLIAM GEORGE PALMER (*J. Soc. Chem. Ind.*, 1920, **69**, 316T).—A simple electrolytic cell of which the essential feature is an inverted, unglazed earthenware pot, which is covered with a parchment paper to act as a diaphragm, is described. The electrodes are of sheet nickel and the electrolyte is a 5—10% solution of potassium hydroxide. W. G.

**The Crystal Lattice of the Hydrogen Haloids.** A. REIS (*Zeitsch. physik.*, 1920, **1**, 299—308).—For the hydrogen haloids, the relation between ionisation energy and molecular volume does not follow the scheme given by Born for the alkali haloids (A., 1919, ii, 214). This relation for the hydrogen haloids is not reconcilable with the assumption of atomic ion lattices, but leads to the assumption of molecular lattices. Further, the inner connexion between the high ionisation energies and the low heats of sublimation of the hydrogen haloids can also only be explained on the assumption of molecular lattices. The lattice structure of the solid hydrogen haloids indicates a very marked unsymmetrical structure of the halogen ions in the molecule of the hydrogen haloids. CHEMICAL ABSTRACTS.

**Action of very Concentrated Solutions of Iodic Acid on Ammonia Gas.** G. DENIGÈS and J. BARLOT (*Bull. Soc. chim.*, 1920, [iv], **27**, 824—825).—It has been shown that, with solutions of iodic acid not exceeding 10% in strength, ammonia gives quadratic crystals of ammonium iodate (this vol., ii, 555). If a drop of a 50% solution of iodic acid is exposed to an atmosphere containing a trace of ammonia gas, it becomes covered with a thin white film, and if this is then well mixed with the iodic acid, rhombic crystals of ammonium tri-iodate can be observed under the microscope. If a drop of 50% iodic acid and a drop of strong ammonium hydroxide are placed a few millimetres apart on a microscope slide, the successive formation of the neutral iodate, the di-iodate, and the tri-iodate may be observed. W. G.

**A New Form of Ozoniser for Laboratory Work.** Y. V. RAMAIAH and M. V. N. SWAMY (*Chem. News*, 1920, **121**, 193).—The ordinary ozone tube is modified by using rarefied gas as a conductor of electricity. The tube through which the air or oxygen passes is enclosed in a glass jacket, in which the air is rarefied by a filter pump, and a second sealed tube, also connected with a filter pump, passes axially through the oxygen tube. The electrodes are small platinum disks attached to wires for the current. In a second form, the outer jacket is of aluminium. A yield of 40—50 mg. of ozone per litre with the first tube, and

50—60 mg. per litre with the second form, was obtained, using dry oxygen.

J. R. P.

**Distillation of a Ternary Mixture, One Constituent of which is not Volatile.** PAUL PASCAL (*Bull. Soc. chim.*, 1920, [iv], 27, 814—820).—A mathematical discussion of work already published (A., 1917, ii, 569). The results are applied to the concentration, by distillation, of nitric acids of different strength.

W. G.

**Hypophosphorous Acid. II. Its Reaction with Iodine.** ALEC DUNCAN MITCHELL (T., 1920, 117, 1322—1335).

**The Crystalline Nature of Graphite and Temper Carbon obtained from Cast Iron.** KEI IOKIBÉ (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, 9, 275—279).—Graphite electrolytically separated from gray pig iron and temper carbon isolated from an annealed white cast iron were compressed into cylindrical rods and the diffraction figures produced by X-rays photographed.

Comparison with the diffraction rings of natural graphite treated in the same way showed that the photographs are identical. Hence it is concluded that temper carbon is not an amorphous substance, but differs only in fineness from natural graphite. Sugar carbon has no crystalline structure, but is an amorphous substance. An attempt to collect temper carbon from quenched carbon steels failed, as its fineness prevented separation by filtration, but since the condition of the decomposition of cementite is the same as in cast iron, the temper carbon in these steels will also be graphite.

T. H. B.

**Poisonous Gases from Carbon Tetrachloride Fire Extinguishers.** A. C. FIELDNER, S. H. KATZ, S. P. KINNEY, and E. S. LONGFELLOW (*J. Franklin Inst.*, 1920, 190, 543—565).—When liquid carbon tetrachloride is poured on to a fire or on to hot metal, or when the vapour is passed, together with air, through a heated iron or quartz tube, it is largely decomposed, with the formation of carbonyl chloride, free chlorine, and hydrogen chloride. At 600° the vapour decomposed much more readily in contact with iron or iron oxide than when in contact with a substance, such as quartz, chemically inert to it. Moisture promoted the formation of carbonyl chloride. At 600° none was formed in dry air in contact with quartz, but in contact with iron covered with oxide 8.3% of the chlorine of the carbon tetrachloride was converted into carbonyl chloride. The effect of iron oxide in promoting the decomposition was greater than that of water-vapour. In the experiments in the quartz tube at 800° a greater amount of the products of decomposition was formed than at 600°, whether moisture was present or not. At 800° carbonyl chloride was produced, even in dry air, in accordance with the equation  $2\text{CCl}_4 + \text{O}_2 = 2\text{COCl}_2 + 2\text{Cl}_2$ . The presence of turpentine vapour in the mixture of carbon tetrachloride vapour and air had an inhibiting

effect on the formation of free chlorine, but little, if any, influence on the production of carbonyl chloride. In analysing the gaseous products, chlorine was estimated by passing the gas through potassium iodide solution, and titrating the liberated iodine; whilst hydrogen chloride was estimated by aspirating the gas through alcoholic alkali hydroxide solution and titrating the total chloride formed, and deducting the amounts due to the chlorine and carbonyl chloride. For the estimation of the carbonyl chloride the gas was passed through silver nitrate on granular pumice to remove hydrogen chloride; then through antimony trisulphide on glass wool to remove chlorine; and finally through a solution of sodium hydroxide in 85% alcohol, and the sodium chloride estimated volumetrically. [See *J. Soc. Chem. Ind.*, 1920, 800A.]

C. A. M.

**The Preparation and Physical Properties of Carbonyl Chloride.** RALPH HALL ATKINSON, CHARLES THOMAS HEYCOCK, and SIR WILLIAM JACKSON POPE (*T.*, 1920, 117, 1410—1426).

**The Preparation of Thiocarbonyl Chloride from Thiocarbonyl Tetrachloride.** PERCY FARADAY FRANKLAND, FREDERICK HORACE GARNER, and DOROTHY WEBSTER (*J. Soc. Chem. Ind.*, 1920, 39, 313—315T).—For the preparation of thiocarbonyl chloride by reduction of thiocarbonyl tetrachloride, tin and hydrochloric acid as reducing agent gave the best results, the yield of thiocarbonyl chloride usually being 55—60%, whilst from 20—35% of the thiocarbonyl tetrachloride was recovered. The best and most economical proportions of tin and acid to use are: 550 grams of thiocarbonyl tetrachloride, 175 grams of tin, and 500 c.c. of a mixture of equal volumes of commercial hydrochloric acid and water, the tetrachloride being added as rapidly as is consistent with efficient condensation of the distillate.

W. G.

**Preparation of Pure Carbon Dioxide.** ROBERT CROSBIE FARMER (*T.*, 1920, 117, 1446—1447).

**Dilatation and Compressibility of Liquid Carbon Dioxide.** C. F. JENKIN (*Proc. Roy. Soc.*, 1920, [A], 98, 170—182).—The compressibility of liquid carbon dioxide was measured from  $-37^{\circ}$  to  $+30^{\circ}$  up to pressures of 100 kilos. per sq. cm. The specific volumes, coefficients of expansion, and coefficients of compressibility are given in tables and curves.

J. R. P.

**A New Form of Silicic Acid.** ROBERT SCHWARZ and OTTO LIEDE (*Ber.*, 1920, 53, [B], 1680—1689).—By leading silicon fluoride into boiling water a form of silicic acid is precipitated, having properties which distinguish it from the product obtained by carrying out the reaction in the cold, or by the hydrolysis of silicon chloride by cold or hot water. The normal product is called  $\alpha$ -silicic acid and the new form  $\beta$ -silicic acid. The  $\beta$ -acid, like the  $\alpha$ -acid, when first precipitated contains about 95% of water, and

when dried over sulphuric acid about 10%. The  $\beta$ -acid dissolves much more slowly in hydrofluoric acid, in sodium hydroxide, or ammonia solution than the  $\alpha$ -acid, and is scarcely coloured by methylene-blue, for which the  $\alpha$ -acid has strong absorptive properties.

The conductivity of ammonia solutions of the  $\beta$ -acid was studied, and compared with that of solutions of the  $\alpha$ -acid. Expressing the quotient of the increase of conductivity occasioned by the dissolved silicic acid,  $\Delta_x$ , and the concentration,  $m$ , by  $Q$ , it is found that, under different conditions, the value of  $Q \times 10^4$  for the  $\beta$ -acid may be 15 or 25, whilst for the  $\alpha$ -acid it is 50 or 75. For freshly prepared, hydrated  $\beta$ -acid  $Q=25$ , and for the aged or dehydrated  $\beta$ -acid,  $Q=15$ . In the  $\beta$ -acid the primary particles are probably larger than in the  $\alpha$ -acid, and the former acid in ammonia probably forms a more highly polymerised polysilicate. E. H. R.

**The Effect of Various Ionogens on the Time Period Required for the Gelation of Colloidal Silicic Acid.** LOUIS F. WERNER (*J. Amer. Pharm. Assoc.*, 1920, **9**, 501—508).—Acids have a very powerful peptising effect on sol colloidal silicic acid. In the case of the strong acids this effect is most marked at medium concentrations. Alkalis also have a strong peptising influence; the effect is greatest at medium to low concentrations for the highly ionised bases, and in the case of the slightly ionised bases the effect is great in all but the lowest concentrations tried. Salts have no effect in presence of acids, but in presence of bases the congealing effect is hastened. The potassium salts of several negative radicles decreased the time required for gelation. The chlorides of various metals, with the exception of ferric and cupric chlorides, decreased the time of gelation. Disodium and monosodium phosphates have strong congealing powers, but trisodium phosphate has the opposite effect. Di- and tri-sodium citrates accelerate the setting greatly, the effect decreasing with the concentration, but in the case of the monosodium salt the time for setting is the same for all concentrations. The acetates of the various metals have the greatest congealing effect (excepting mercury). Inorganic salts produce but little effect. The alkali salts of the organic acids produce powerful accelerating effects, except the carbonates and hydrogen carbonates, which have a peptising effect in medium to dilute solutions. CHEMICAL ABSTRACTS.

**Constitution of the Silicates.** JOHANN JAKOB (*Helv. Chim. Acta*, 1920, **3**, 669—704).—The author discusses the general principles underlying the structure of the silicates and develops systematically the formulæ of silicates of the most varied type, starting with the simplest and proceeding to those of gradually increasing complexity. The nomenclature of the different compounds is likewise considered.

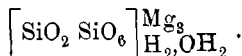
The classes into which the silicates are divided are as follows:  
I. Silicates with simple silicic acid ions: (1) Hexaoxy-silicates, such

as asperolith,  $\left[\text{SiO}_6\right]_{\text{H}_6}^{\text{Cu}}$ ,  $\left[\text{SiO}_6\right]_{\text{Mg}(\text{Fe})}^{\text{Al}_2}$ , dumortierite,  $[\text{SiO}_6]_3\text{Al}_8$ .

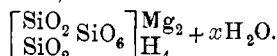
(2) Pentaoxy-silicates, such as andalusite,  $[\text{SiO}_5]\text{Al}_2$ , titanite,  $\left[\text{SiO}_5\right]_{\text{Ti}}^{\text{Ca}(\text{Fe})}$ . (3) Tetraoxy-silicates ("orthosilicates"), such as

diopside,  $\left[\text{SiO}_4\right]_{\text{H}_2}^{\text{Cu}}$ . II. Silicates with complex silicic acid ions:

(1) Monosilicohexaoxysilicates, such as serpentine,

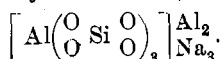


(2) Disilicohexaoxysilicates, such as meerschaum,

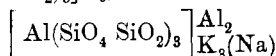


(3) Trisilicohexaoxysilicates, such as the pyroxenes and many of their products of hydrolysis, for instance, talc,  $\left[\text{Si}\left(\begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} \text{ Si } \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} \right)_3\right]_{\text{H}_6}^{\text{Mg}_3}$ .

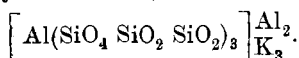
(4) More highly silicated hexaoxysilicates, as yet unknown. III. Silicato-salts: (1) Tetraoxysilicato-salts, such as nepheline,



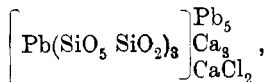
(2) Pentaoxysilicato-salts, of which sillimanite,  $[\text{Al}(\text{SiO}_5)_3]\text{Al}_5$ , possibly represents the type. (3) Hexaoxysilicato-salts, for example, dumortierite,  $[\text{SiO}_6]_4\text{Al}_8$ . (4) Trisilicotetraoxysilicato-salts of the type  $[\text{Al}(\text{SiO}_4 \text{ SiO}_2)_3]\text{R}_9$ , such as leucite,



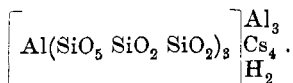
(5) Hexasilicotetraoxysilicato-salts, such as orthoclase,



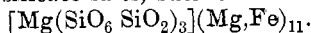
(6) Trisilicopentaoxysilicato-salts, to which rasonite,



and ganomalite,  $\left[\text{Pb}(\text{SiO}_5 \text{ SiO}_2)_3\right]_{\text{Ca}_3, \text{Ca}(\text{OH})_2}^{\text{Pb}_5}$ , probably belong. (7) Hexasilicopentaoxysilicato-salts, such as pollux,



(8) Trisilicohexaoxysilicato-salts, such as olivine,



(9) More highly silicated silicato-salts,  $[\text{Al}(\text{SiO}_6 \text{ SiO}_2 \text{ SiO}_2)_3]\text{R}_{21}$ , as yet unknown. IV. Co-ordination compounds of the highest order, in which, not an atom, but an atomic grouping, appears as co-ordination centre; to this class belongs tourmaline (Reiner, A., 1913, ii, 718; Wülfing and Becht, A., 1914, ii, 63).

Many types of these silicate compounds are able to crystallise both with and without water of crystallisation; this deposition of water molecules is fundamentally a partial regeneration of complex hydrate ions, such regeneration rendering possible subsequent dissociation or hydrolysis.

T. H. P.

**Application of a New Physico-chemical Volumetric Method.** RENÉ DUBRISAY (*Compt. rend.*, 1920, 171, 670—672).—Applying the method previously described (A., 1919, i, 73; ii, 78) to the study of the neutralisation of sulphuric acid, the author finds a point of inflexion on the curve corresponding with the formation of sodium hydrogen sulphate and another at the point where the normal salt is obtained.

With solutions of sodium sulphate and sulphuric acid the difference between the observed and calculated temperatures reaches a maximum when the solutions are mixed in equimolecular proportions. The same holds good for solutions of sodium sulphate and hydrochloric acid.

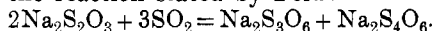
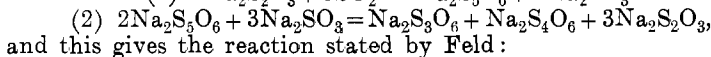
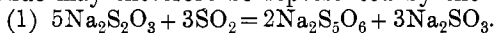
W. G.

**Crystal Structure of Sodium Nitrate.** RALPH W. G. WYCKOFF (*Physical Rev.*, 1920, 16, 149—157).—Laue photographs were taken through crystals of sodium nitrate normal and slightly inclined to the (111) and (100) face. It is found, using a method of interpretation similar to that of Nishikawa, that the crystal can be referred to a set of interpenetrating rhombohedral lattices with axes which are the diagonals of the plane formed by taking the usual crystallographic axes as edges. The lattice arrangement thus found is that anticipated by Bragg on the basis of partial measurements, and is essentially the same as that of calcium carbonate, that is, may be regarded as similar to that of sodium chloride with  $\text{NO}_3$  groups replacing the chlorine atoms. The co-ordinates of the atoms, assuming the length of the sides of the unit rhombohedron to be 1, are sodium at  $(0, 0, 0)$ , and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ ; nitrogen at  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$  and  $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ ; oxygen at  $(\beta, 1-\beta, 0)$ ;  $(0, \beta, 1-\beta)$ ;  $(1-\beta, 0, \beta)$ ;  $(\frac{1}{2}-\beta, \beta-\frac{1}{2}, \frac{1}{2})$ ;  $(\beta-\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-\beta)$ ;  $(\frac{1}{2}, \frac{1}{2}-\beta, \beta-\frac{1}{2})$ , where  $\beta$  is very nearly  $\frac{1}{4}$ .

CHEMICAL ABSTRACTS.

**The Production of Ammonium Sulphate from Coke-oven Gases by the Feld Process.** F. RASCHIG (*Zeitsch. angew. Chem.*, 1920, 33, 260—262).—By the Feld process (A., 1912, ii, 448) both hydrogen sulphide and ammonia are recoverable from coke-oven gases with production of ammonium sulphate. The operations comprise treatment of the gases with aqueous solutions of ammonium trithionate and tetrathionate, recovery of these from the thiosulphate formed by the action of sulphur dioxide, and their decomposition on boiling into ammonium sulphate, sulphur dioxide, and sulphur, followed by oxidation of the sulphur. In regard to the reaction  $4(\text{NH}_4)_2\text{S}_2\text{O}_8 + 6\text{SO}_2 = 2(\text{NH}_4)_2\text{S}_3\text{O}_6 + 2(\text{NH}_4)_2\text{S}_4\text{O}_6$ , examination of the behaviour of analogous sodium compounds shows that with dilute solutions, only sulphite and

sulphate with traces of polythionates are formed. If the solution is very concentrated, the conversion into the polythionates proceeds rapidly. During an investigation of the polythionates it was discovered that by interaction with sodium sulphite, penta- and tetrathionate are converted into trithionate and thiosulphate:  $\text{Na}_2\text{S}_5\text{O}_6 + 2\text{Na}_2\text{SO}_3 = \text{Na}_2\text{S}_3\text{O}_6 + 2\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{Na}_2\text{S}_4\text{O}_6 + \text{Na}_2\text{SO}_3 = \text{Na}_2\text{S}_3\text{O}_6 + \text{Na}_2\text{S}_2\text{O}_3$ ; treatment of the trithionate with sulphite fails to yield dithionate, which is therefore not a true polythionate. The decomposition of acid solutions of thiosulphates into sulphurous acid and sulphur is not quantitative, and is accompanied by the formation of pentathionate owing to polymerisation of the thiosulphate. This effect is increased by addition of a trace of an alkali arsenite as a catalyst. In practice, the treatment of the thiosulphate with sulphur dioxide may therefore be represented by the equations:



The reactions have been based on proportions of ammonia and hydrogen sulphide of 2:1. With excess of ammonia the recovery of the thionates is retarded, and more hydrogen sulphide must be introduced into the gases. A preponderance of hydrogen sulphide necessitates partial oxidation to sulphur.

W. J. W.

### The Melting and Boiling Points of Ammonium Sulphate.

E. JÄNECKE (*Zeitsch. angew. Chem.*, 1920, **33**, 278—280).—The equilibrium relations between sulphuric acid, ammonia, and acid and normal ammonium sulphates have been investigated, and the results obtained have been plotted on curves. At atmospheric pressure it is shown that the hydrogen sulphate,  $(\text{NH}_4)\text{HSO}_4$ , has m. p.  $251^\circ$  and b. p.  $490^\circ$ , and the normal sulphate,  $(\text{NH}_4)_2\text{SO}_4$ , has the same m. p. and b. p.  $357^\circ$ . The eutectic mixture has m. p.  $195^\circ$ . The author pleads for more investigations of the physical properties of the common chemicals in everyday use.

A. J. H.

### Fusion of Zinc, Cadmium, and Mercury Sulphides.

ERICH TIEDE and ARTHUR SCHLEEDER (*Ber.*, 1920, **53**, [B], 1717—1721).—These sulphides, which sublime without melting under atmospheric pressure, have been obtained in the molten condition by heating in a carbon-tube pressure furnace in an atmosphere of nitrogen. Zinc sulphide melted under 100—105 atm. at  $1800$ — $1900^\circ$ . The solidified fused sulphide had a lustrous appearance and a bright greenish-yellow colour; it proved to be the hexagonal modification. Cadmium sulphide was fused at 100 atm. at about  $1750^\circ$ ; the fused solid had a dark brownish-yellow colour and lustrous appearance. Mercuric sulphide was fused at 120 atm. and  $1450^\circ$ . The fused solid had a steel-grey, matt appearance, and, when rubbed, quickly became red.

E. H. R.

### Thermochemical Analyses of Solutions.

E. CHAUVENET, P. JOB, and G. URBAIN (*Compt. rend.*, 1920, **171**, 855—857).—The

method used is similar to that described by Dubrisay (this vol., ii, 508), and by its use the existence of the double salts  $2\text{KI}, \text{CdI}_2$ ;  $2\text{CuCl}_2, 3\text{MgCl}_2$ ;  $3\text{CuCl}_2, 2\text{MgCl}_2$ ;  $2\text{CuCl}_2, 3\text{CaCl}_2$ ;  $\text{CuCl}_2, \text{CaCl}_2$ ;  $\text{CuCl}_2, 2\text{AlCl}_3$  and  $2\text{CuCl}_2, \text{AlCl}_3$  is shown.

W. G.

**Lead Hydride.** FRITZ PANETH and OTTO NÖRRING (*Ber.*, 1920, 53, [B], 1693—1710).—The methods previously employed for the detection of the hydrides of bismuth (*A.*, 1919, ii, 67, 68) and tin (this vol., ii, 41) have been applied in the study of the possibility of the existence of a hydride of lead. Magnesium powder was activated with thorium-*B* and thorium-*C* in a desiccator for half-an-hour and was then dissolved in 0.1 or 0.2*N*-hydrochloric acid, the resulting gases being carried in a stream of hydrogen through a cotton-wool filter to a heated Marsh tube. The radioactivity of the metallic deposit, consisting chiefly of thorium-*C* (bismuth), was then examined. For the first few hours its behaviour was indistinguishable from that of thorium-*C*, but after twenty-four hours, by which time the thorium-*C* should have disappeared, a notable activity remained, the rate of disappearance of which corresponded with that of thorium-*B* (lead). The "yield" of lead obtained, however, was only about one hundredth that of the bismuth. The lead hydride appeared to be stopped or decomposed more readily by a thick cotton-wool filter than bismuth hydride.

Attempts to prepare the hydride by the action of acids on ordinary lead-magnesium alloys were unsuccessful, and so were numerous attempts by electric methods, for example, induction sparks or an arc in an atmosphere of hydrogen. Success was eventually attained by a combined electrolysis-spark process in a specially designed apparatus. Using dilute sulphuric acid as electrolyte and a lead-glycerol cement cathode, with an *E.M.F.* of 220 volts, the apparatus was so arranged that intermittent sparking at high frequency occurred between the cathode and the electrolyte. The cathode gases were passed to a condensing tube immersed in liquid air where any lead dust was deposited, whilst the hydride was liquefied. On allowing the temperature to rise, the hydride was again vapourised and passed through a cotton-wool filter to a heated Marsh tube, where it was decomposed and lead deposited. The deposit had a dull grey colour, and was close to the flame, but not so close as a tin deposit. The lead was identified by a number of chemical tests which distinguished it from arsenic, antimony, tin, tellurium, or bismuth. A number of modifications of the experiment indicated that the hydrogen required for the formation of the hydride is not derived from the electrolysis of the electrolyte, but probably through the action of the spark, positive hydrogen ions combining directly with negative lead ions. So-called active hydrogen may play a part in the reaction.

E. H. R.

**Combinations of Haloid Derivatives of Lead and Thallium.** BARLOT (*Compt. rend.*, 1920, 171, 794—796).—Conductivity measurements show the existence of double chlorides,



*bromides* and *iodides* of lead and thallium having the general formula  $TlX, PbX_2$ , and the author has obtained all of these in a crystalline form. There are indications of the existence of a second double chloride,  $2TlCl, PbCl_2$ , but this could not be isolated. W. G.

**Thermal Analysis of the System Thallium Nitrate: Thallium Nitrite.** VITTORIO CUTTICA (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 89—92. Compare Rolla and Belladen, this vol., ii, 34).—The thermal behaviour of fused mixtures of thallium nitrate and nitrite excludes the formation of complexes. The two salts form an uninterrupted series of mixed crystals, the transformation in the solid state corresponding with Roozeboom's type II.

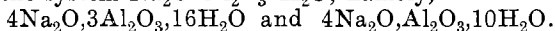
T. H. P.

**Study of the Transformation Points by a Dilatometric Method.** PAUL BRAESCO (*Ann. Physique*, 1920, [ix], **14**, 5—75).—The first part of the paper is a detailed account of work already published (A., 1919, ii, 153). The method has been applied to the study of alloys and by means of it the author has proved the existence of the definite copper-antimony compound  $Cu_3Sb$ . With copper-aluminium alloys, the phenomena of tempering are particularly well shown by this method. In the case of the bronzes, the allotropic transformation of the compound  $Cu_4Sn$  was observed and also the transformation  $\beta \rightarrow \alpha + \delta$ . W. G.

**Determination of the Atomic Weight of Thulium.** C. JAMES and O. J. STEWART (*J. Amer. Chem. Soc.*, 1920, **42**, 2022—2023).—The atomic weight of thulium has been determined from the ratio  $TmCl_3 : 3Ag$  from three specimens of thulium obtained as described previously (A., 1911, ii, 891). The experimental procedure was identical with that followed in the determination of the atomic weight of samarium (A., 1918, ii, 44). The purest fraction gave a value 169.44 for the atomic weight as a mean of three determinations, whilst the other two fractions, which contained neoytterbium, gave 169.66 and 169.90 respectively.

J. F. S.

**Sodium Aluminates. Equilibria in the System  $Na_2O-Al_2O_3-H_2O$ .** F. GOUDRIAAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 129—142).—At  $30^\circ$ , two stable aluminates occur in the system  $Na_2O-Al_2O_3-H_2O$ , namely,



Both form incongruently saturated solutions, that is, are decomposed by water and dilute sodium hydroxide solution. According to the mode of preparation, aluminium hydroxide may be obtained in different forms. Under special conditions, alumina forms a crystalline hydrate,  $Al_2O_3 \cdot 3H_2O$ . The gelatinous hydroxide must be considered as a metastable phase of variable composition. It adsorbs variable quantities of alkali. There is very probably a continuous transition between these gelatinous hydroxides and the crystalline hydrate. Aluminium oxide is metastable at  $30^\circ$  in

respect of the hydrate. The swelling exhibited by the desiccated particles of hydroxide and oxide is dependent on the alkalinity of the solution.

J. R. P.

**The Equilibrium-diagram of Carbon-Manganese Alloys.**

K. KIDO (*Sci. Rep. Tôhoku. Imp. Univ.*, 1920, **9**, [iv], 305—310).—The object of this investigation was to establish the equilibrium diagram of manganese and carbon with a high degree of certainty.

A series of alloys was prepared by diluting with manganese the carbide  $Mn_3C$ , made in an electric furnace. In the liquid state, the carbide and manganese are soluble in all proportions, but only partly in the solid state. The saturation points of carbide in manganese and manganese in carbide were determined. As the temperature falls, the solubility of both decreases, and they form a eutectoid having a composition of about 3.7% C. Specimens quenched at different temperatures and subjected to micro-examination showed that the eutectoid temperature is a little above  $900^\circ$ , and the transformation takes place at a somewhat lower temperature during cooling than on heating. Thermal analysis confirmed this, showing an absorption of heat above  $900^\circ$  during heating and an evolution of heat at about  $830^\circ$  on cooling.

T. H. B.

**The Point  $A_r$  of Steels, and Martensite.**

P. DEJEAN (*Compt. rend.*, 1920, **171**, 791—794).—A review of his previous work (compare A., 1917, ii, 477) in the light of recent work by Guillet (*Rev. gén. Sci.*, 1920, **31**, 496).

W. G.

**Metal Tubes which are Stable towards Water Vapour at Temperatures above  $1000^\circ$ .**

PAUL ASKENASY (*Zeitsch. Elektrochem.*, 1920, **26**, 436).—Tubes made from silicised iron sheet are very little attacked by air, or mixtures of steam and oxygen at temperatures of  $1100^\circ$ . The metal is brittle, but by careful heating may be raised to a red heat and can then be bent into a tube which can be welded by the autogenous method. Such tubes, when surrounded by cast iron, serve well as superheaters for steam. Chromium nickel tubes are equally resistant to steam at high temperatures.

J. F. S.

**Hydrous Oxides. I. and II.**

HARRY B. WEISER (*J. Physical Chem.*, 1920, **42**, 277—328, 505—538).—1. HYDROUS FERRIC OXIDE.—A survey of investigations on the composition of colloidal ferric oxide has been made. The existence of no definite basic ferric salt has been established with certainty, and only one definite crystalline hydrate has been prepared. The latter is formed only under special conditions, namely, the decomposition of sodium ferrite by water at the ordinary temperature. It is probable that the different ferric iron colloids are not composed of basic salts of varying composition or of hydrous hydrated oxides, but are hydrous ferric oxide. The difference in properties of colloidal

hydrous ferric oxides prepared by different methods and of different ages is due to a difference in the degree of hydration and in the size of the colloidal particles. It is unnecessary to postulate the existence of basic chlorides or complex salts of varying composition in order to account for the existence of only a part of the chlorine in the dialysed Graham colloid as the chloride ion.

Certain electrolytes precipitate the Péan de St. Gilles colloid in a gelatinous form, whilst others precipitate it in a granular form. The nature of the precipitate depends on the conditions of precipitation; the same electrolyte may produce either a granular or gelatinous mass in suitable circumstances. The most gelatinous precipitate is obtained when there is very rapid aggregation of the hydrous particles throughout the entire solution and when the electrolyte present exerts no solvent action; the most granular precipitate results when the agglomeration proceeds slowly and when the electrolyte possesses a solvent action.

The influence of the valencies of the ions of the precipitating electrolytes was investigated.

Hydrochloric acid has two precipitating values for the Péan de St. Gilles colloid, one above the other with a zone of non-precipitation between, in which the colloid is less stable than the original colloid. The degree of reversibility of the precipitation of hydrous ferric oxide is determined mostly by the specific adsorbability of the precipitating ion, although the physical character of the precipitate has an influence.

It is not probable that the different colours of hydrous ferric oxide (reddish-brown, yellow, and red) are due to complex salts or hydrous hydrated oxides, since it is possible to make a transition from brown to yellow by increasing the size of the particles. This may be effected by heating water to which ferric chloride has been added. The yellow colloidal hydrous oxide is not readily dehydrated at  $100^{\circ}$  and probably contains adsorbed ferric salt.

A yellow colloidal solution was prepared by the Péan de St. Gilles method by allowing the acetate solution to remain for a few days before diluting and boiling. The slow hydrolysis of the acetate favours the formation of yellow hydrous oxide stabilised by adsorbed ferric salt. When the solution is boiled, a stable yellow colloid is formed instead of the usual brick-red.

II. HYDROUS ALUMINIUM OXIDE.—Aluminium oxide forms only one definite hydrate, the trihydrate, precipitated from solutions of the oxide in alkali. The so-called hydrates formed by precipitating with ammonia are hydrous oxides. Any number of hydrous oxides, similar to those of ferric oxide, may be prepared, differing in size of particles and amount of water. The larger and less hydrous the particles, the less soluble are they in acids and alkalis. There is no temperature of inversion from soluble oxide to insoluble meta-oxide. The colloidal oxide prepared by prolonged digestion of aluminium acetate at high temperature is insoluble in acids and alkalis and has no mordanting action; the

colloid prepared by peptising gelatinous alumina with aluminium chloride and dialysing in the cold is soluble in acids and alkalis and possesses a mordanting action. Colloids with intermediate properties may be obtained.

Colloidal alumina is a positive colloid and is stabilised by preferential adsorption of cations. The relative peptising power at  $100^{\circ}$  was found to be in the order: nitric acid > hydrochloric acid > ferric chloride > aluminium chloride > acetic acid. It is probably incorrect to assume the formation of aluminium ion as an intermediate step in the peptisation of aluminium oxide by acids and salts. The colloids formed by peptisation of gelatinous alumina are not composed of basic salts of varying composition, neither is there any necessity to assume the formation of a series of hypothetical complex salts to account for the properties of the colloid.

The coagulation of colloidal aluminas by electrolytes was studied. Strong acids with univalent anions and their salts precipitate the colloid only at high concentrations and the reaction is reversible. Acids with multivalent anions and their salts precipitate the colloid at low concentrations and irreversibly. Rose's explanation of the cause of the reversibility of precipitation is shown to be untenable. Gelatinous alumina dissolves in sodium or potassium hydroxide with the production of an unstable aluminate, from which colloidal hydrated alumina separates in a granular, sparingly soluble form. Observation of the effect of the nature of the coagulating agent on the physical character of the precipitated oxide confirmed the conclusions reached with ferric oxide.

J. R. P.

### **The Double Colloidal Sulphide of Iron and Sodium.**

S. M. HORSCH (*Bull. Soc. chim.*, 1920, [iv], **27**, 777—779).—When hydrogen sulphide is passed over a molten mixture of sodium hydroxide and ferric oxide, a double sulphide,  $\text{FeS}_4\text{Na}_2\text{S}$ , is obtained, which dissolves in water, giving a deep emerald-green solution. Its aqueous solution, after dialysis, in the absence of air, retains the two sulphides in the proportion given. A concentrated solution on cooling gives a hydrogel, having the composition  $\text{Na}_2\text{S}, 2\text{FeS}$ , which dissolves in water, giving a black solution, and on adding ammonium chloride to this solution, ferrous sulphide is precipitated. If to this solution the requisite amount of sodium sulphide is added, it regains the original green colour.

W. G.

### **The Stability of the Cobaltamines.**

ARTHUR B. LAMB and ALFRED T. LARSON (*J. Amer. Chem. Soc.*, 1920, **42**, 2024—2046).—The six cobaltamines examined were aquopentamminecobalt chloride, diaquotetramminecobalt chloride, 1:2-dinitrotetramminecobalt chloride, nitropentamminecobalt chloride, hexamminecobalt chloride, and 1:6-dinitrotetramminecobalt chloride. The oxidation potentials of aqueous solutions of these amines in 3.265*M*-ammonium hydroxide solution were

measured, and from these results the concentrations of the simple cobaltic ions in these solutions were calculated, thus giving a measure of the relative stability of the ammines. They are arranged above in order of descending stability.

The potentials of the cobalt-cobaltous electrode in cobaltic chloride solution and in ammoniacal cobaltic chloride solutions were measured, and from these results the formula of the aminocobaltous ion in the presence of excess of ammonia is shown to be  $\text{Co}(\text{NH}_3)_6^{++}$ . The equilibrium constant for its dissociation into ammonia and simple cobaltous ions has been calculated.

The value for the cobaltous-cobaltic potential, as redetermined, is 1.775 volts at  $0^\circ$  with a temperature-coefficient of  $+0.00169$  volt.

W. G.

**Influence of Chromium Compounds on the Corrosion of Iron.** GEORGE W. HEISE and AMANDO CLEMENTE (*Philippine J. Sci.*, 1920, **16**, 439—446).—Passivifying agents, such as potassium dichromate, may increase the corrosion of iron in salt solutions, owing to formation of free acid, and the depolarising effect of the dichromate:  $\text{H}_2\text{O} + \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl} \rightleftharpoons \text{K}_2\text{CrO}_4 + \text{Na}_2\text{CrO}_4 + 2\text{HCl}$ . Experiments were carried out to determine the influence on corrosion produced by increasing amounts of potassium dichromate added to sulphuric acid of various strengths. With  $N/2$ -sulphuric acid corrosion was accelerated proportionately to the amount of dichromate added up to a concentration of above 19 grams, at which stage the iron became passive; with further additions of dichromate corrosion gradually diminished. With  $N$ -acid the passive condition was more indefinite, but was reached in individual cases with a concentration of 50 grams per litre. Increase of corrosion up to this point, and decrease beyond it, occurred as with  $N/2$ -acid. In the case of  $2N$ -acid no passive state was reached even when a saturated solution of dichromate was employed, and corrosion was accelerated by the addition of increasing amounts of the salt.

The addition of a small amount of potassium dichromate and potassium chromate to 10% sulphuric acid at first increased the corrosion of iron, but after reduction of the salt had taken place no further effect occurred with increased time of treatment. Chromium sulphate or chloride is apparently without influence on the rate of corrosion, the results obtained by Watts (*Trans. Amer. Electrochem. Soc.*, 1912, **21**, 337—353) not being confirmed. Differences in the iron used and in the acid concentration may account for this divergence.

W. J. W.

**The Precipitation of Tin by Iron.** I. M. KOLTHOFF (*Rec. trav. chim.*, 1920, **39**, 606—608).—A reply to Bouman (this vol., ii, 547).

W. G.

**The Solubility of Earth-acid Gels [Titanic, Tantallic, and Columbic Acids] in Hydrogen Peroxide-Acid Mixtures.** OTTO HAHN and HANS GILLE (*Zeitsch. anorg. Chem.*, 1920, **112**, 283—292).—For the separation of titanic, tantallic, and columbic

acids from most other elements, a method was given by Weiss and Landecker (A., 1909, ii, 942) which consisted in dissolving the acids, whether precipitated from acid or basic solutions, in hydrogen peroxide and reprecipitating by boiling the solution with sulphurous acid. Experiments on the solubility of these acids in acid solutions of hydrogen peroxide have not confirmed Weiss and Landecker's statements. The acids used for the experiments were prepared by fusing the commercial material with sodium hydrogen sulphate, extracting with boiling water, and hydrolysing the solutions by boiling with sulphurous acid. Titanic and columbic acids are practically completely soluble in acid hydrogen peroxide, but tantalic acid when precipitated hot is almost insoluble, and when precipitated cold is only partly soluble. In mixtures, the different acids influence one another differently according to the conditions. Tantalic acid lowers the solubility of columbic acid, whilst titanic acid may increase the solubility of tantalic acid or may itself be rendered less soluble. Experiments with the ultra-microscope indicate that, in acid hydrogen peroxide solutions, titanic acid forms a true solution, whilst columbic and tantalic acids form colloidal solutions.

E. H. R.

### **Colloidal Sulphur Compounds of Ruthenium.** F. M.

JAEGER and J. H. DE BOER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 95—102).—The product of the precipitation of a salt of quadrivalent ruthenium by ammonium sulphide differs with the temperature. At 100° brownish-black  $\text{RuS}_2$  is formed, together with free sulphur, but at 0° greenish-black  $\text{RuS}_6$  is formed, which has the character of an irreversible colloid and with excess of ammonium sulphide gives a green, unstable colloidal solution. At intermediate temperatures mixtures of both sulphides and free sulphur are formed. The dark green sulphide and the green colloidal solution of  $\text{RuS}_6$  (containing positively charged particles) rapidly absorb free oxygen, forming a reddish-violet solution of the reversible colloid ruthenium pyrosulphite,  $\text{Ru}_4\text{S}_4\text{O}_{10}$ , the particles of which are positively charged. This salt is in turn converted by oxygen (air, nitric acid, permanganate) into ruthenium sulphate and free sulphuric acid. The properties and reactions of the products were investigated.

J. R. P.

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### Mineralogical Chemistry.

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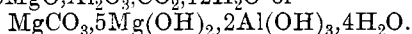
**The Nomenclature and Classification of Sulphide Minerals.** EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1920, 10, 487—496).—A tabular classification is given on much the same lines as that of Dana's "System of Mineralogy" (6th edit., 1892),

but in greater detail. Several incompletely described minerals are listed. In addition to selenides, tellurides, arsenides, antimonides, and bismuthides, there are also included the few naturally occurring oxysulphides, nitrides, phosphides, carbides, and silicides.

L. J. S.

### Composition of Minerals of the Hydrotalcite Group.

WILLIAM F. FOSHAG (*Proc. U.S. Nat. Mus.*, 1920, **58**, 147—153).—Hydrotalcite from Kongsberg, Norway, consisting of curved lamellar masses with white colour and pearly lustre, gave anal. I, agreeing with  $6\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 12\text{H}_2\text{O}$  or



This mineral is thus a basic carbonate rather than a hydrated oxide, as previously regarded. It glows intensely before a blowpipe, becoming silvery-white, but does not fuse. Stichtite (of W. F. Petterd, 1910 = Chrom-brugnatellite of L. Hezner, A., 1912, ii, 1061) from the original locality in Tasmania, gave II, agreeing with the analogous formula  $6\text{MgO} \cdot \text{R}_2\text{O}_3 \cdot \text{CO}_2 \cdot 12\text{H}_2\text{O}$ . Before the blowpipe it glows intensely, turns light grey, and becomes magnetic, but does not fuse.

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Cr <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	CO <sub>2</sub> .	H <sub>2</sub> O.	Total.
I. 0.44	15.32	—	1.89	0.28	nil	39.72	7.60	35.46	100.71
II. 2.09	2.24	14.08	4.04	0.28	trace.	36.59	6.94	33.01	99.27

Previous analyses of pyroaurite suggest that the formula for this should be  $6\text{MgO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{CO}_3 \cdot 12\text{H}_2\text{O}$ . A new estimation of ferrous iron in pyroaurite from Långban, Sweden, gave FeO 0.74%. These minerals all possess a perfect basal cleavage, and are optically uniaxial with weak birefringence. Brugnatellite (A., 1909, ii, 247) probably belongs to the same group, and may be identical with pyroaurite. Hydrotalcite, stichtite, and pyroaurite result from the alteration of corresponding members of the spinel group, namely, spinel, chromite, and jacobsonite respectively.

L. J. S.

**Vonsenite, a New Mineral.** ARTHUR S. EAKLE (*Amer. Min.*, 1920, **5**, 141—143).—A large boulder-shaped mass of a coal-black mineral with brilliant, metallic lustre occurs with magnetite, chlorite, and pyroxene at a granite limestone contact at Riverside, California. It is quite opaque and non-magnetic; H 5, D 4.21. Imperfect, prismatic crystals are orthorhombic or monoclinic ( $a:b=0.7558$ ). The mineral fuses at 3 to a black, magnetic bead, and it is completely soluble in hydrochloric or sulphuric acid. The average composition is:

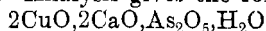
FeO.	MgO.	B <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Total.
39.75	10.71	14.12	34.82	99.40

Other estimations of magnesia gave 7.43—11.51%. These results agree with the ludwigite formula,  $3(\text{Fe}, \text{Mg})\text{O} \cdot \text{B}_2\text{O}_3 + \text{FeO} \cdot \text{Fe}_2\text{O}_3$ , but with ferrous oxide largely in excess of magnesia. Further, the mineral differs structurally and optically from ludwigite. L. J. S.



**Higginsite, a New Mineral of the Olivenite Group.**

CHARLES PALACHE and EARL V. SHANNON (*Amer. Min.*, 1920, **5**, 155—157).—Occurs as bright green, orthorhombic crystals ( $a:b:c=0.6242:1:0.7940$ ) in black manganese ores at the Higgins mine, Bisbee, Arizona. H  $4\frac{1}{2}$ , D 4.33, fusibility 3; readily soluble in hydrochloric or nitric acid, partly soluble in sulphuric acid, and insoluble in ammonia. Analysis gives the formula



or  $\text{CuCa}(\text{OH})(\text{AsO}_4)$ , analogous to those of olivenite and desclozite.

CuO.	CaO.	V <sub>2</sub> O <sub>5</sub> .	As <sub>2</sub> O <sub>5</sub> .	$\frac{\text{H}_2\text{O}}{<105^\circ}$ .	$\frac{\text{H}_2\text{O}}{>105^\circ}$ .	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	Insol.	Total.
28.67	20.83	1.97	41.23	0.08	3.41	0.48	2.84	0.86	100.37

L. J. S.

**Australian Minerals.** C. ANDERSON (*Rec. Australian Museum*, 1920, **30**, 1—31).—Detailed crystallographic descriptions are given of several mineral species from various Australian localities; analyses are given of the following: Corroded crystals of beryl (aquamarine), from Torrington, N.S.W., have low D 2.664 and refractive indices  $\omega=1.5685$ ,  $\epsilon=1.5640$  (Na), and are correspondingly poor in alkalis, as shown by the following analyses by J. C. H. MINGAYE (*Ann. Rep. Dept. Mines, N.S.W.*, 1916, for 1915, 198):

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	GlO.	FeO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.	Sp. gr.
I.	66.08	19.86	12.96	0.30	nil	0.43	nil	0.58	100.21	2.661
II.	64.70	22.22	11.84	0.37	0.04	0.24	0.13	0.60	100.14	2.666

Also traces of Mn, Li, Sr, and Cs (?); absence of Ca, Cr, V, P. Associated with the beryl is wolframite, which, containing only 3.95% MnO, is near the ferberite end of the series. Chabazite (var. phacolite), as small crystals with calcite in decomposed basalt near Glen Innes, N.S.W., gave SiO<sub>2</sub> 45.71, H<sub>2</sub>O 21.91%. Mimetite, as almost white crystals in limonite, from Mount Bonnie, Northern Territory, gave:

PbO.	As <sub>2</sub> O <sub>5</sub> .	P <sub>2</sub> O <sub>5</sub> .	Cl.	Total (less O for Cl).
76.22	20.55	1.41	2.00	99.73

L. J. S.

### **Analytical Chemistry.**

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**A Graduated Tap Funnel for the Acid Incineration Mixture in Neumann's Method.** GEORG LOCKEMANN (*Zeitsch. physiol. Chem.*, 1919, **107**, 211—212).—The manipulation in Neumann's wet method for ashing organic substances (*A.*, 1903, ii, 243; 1905, ii, 68) is facilitated by the use of a graduated tap funnel for running in the acid mixture. S. S. Z.

**Use of Ultrafiltration in Toxicological Analysis.**

C. MANNICH and GRETE WIPPERLING (*Ber. Deut. pharm. Ges.*, 1920, **30**, 348—361).—Ultrafiltration (filtration through collodion membrane) is not suitable generally for toxicological work, owing to loss of alkaloids and heavy metals, due to absorption of these by the membrane. The loss is small, but it is important when dealing with traces of poisons; it is greatest in the case of mercury and practically negligible for arsenic and antimony. The method, however, is useful for the separation of potassium chlorate and oxalic acid from organic substances, etc.

W. P. S.

**Alignment Chart for Reduction of Gaseous Volumes.**

HANS G. SCHWERDT and W. W. LOEBE (*Chem. Zeit.*, 1920, **44**, 818—819).—The construction and use of an alignment (nomographic) chart for the reduction of volumes of gases, measured over water or potassium hydroxide solution, to standard temperature and pressure are described.

J. R. P.

**Exact Gas Analytical Methods.**

E. OTT (*J. Gasbeleucht.*, 1920, **63**, 198—205, 213—220, 246—253, 267—271; from *Chem. Zentr.*, 1920, iv, 397. Compare this vol., ii, 52).—The combustion of carbon monoxide, hydrogen, and methane, separately and when mixed in the presence of platinum, has been examined. The calculation is based on observations of the contraction, carbon dioxide produced, and oxygen consumed. The estimation of a mixture of the three gases by absorption of carbon monoxide by means of cuprous chloride, followed by fractional combustion of hydrogen and methane, has been performed as a control. In addition, the mixed gases are investigated by the fractional combustion of hydrogen and methane on the one hand and of methane on the other in the presence of platinum. The results are fully described, and are designed as standards for a subsequent investigation of the fractional combustion of the gases over copper oxide. A simple apparatus is described which permits the complete analysis of coal-gas, etc., and in which the parts containing the gas remain closed; the estimation of heavy hydrocarbons necessitates the attachment of a connexion for the introduction of liquid, and this can be conveniently arranged.

H. W.

**The Examination of Naturally Occurring Gases.**

F. HENRICH (*Ber.*, 1920, **53**, [B], 1940—1949).—Methods for collecting and analysing natural gases are described. A special apparatus was designed for removing nitrogen for the estimation of the rare gases after removing carbon dioxide and oxygen by the usual methods. The gas is circulated through a hard glass tube, heated at 500°, containing a mixture of calcium and sodium in the ratio 10:1, until there is no further diminution in the volume of the gas. Since the hard glass tube is attacked by the metal and will not stand a vacuum at the temperature employed, it is enclosed in a quartz tube, contact between the two being prevented by means of iron foil or wire. The nitrogen can by this

means be removed completely from about 300 c.c. of gas in from ten to fifteen minutes. The gas from a cold spring near Leupoldsdorf, Bavaria, was found to contain 13.0% of oxygen, 86% of nitrogen, and 1% of rare gas, chiefly argon. Its radioactivity was  $0.2398 \cdot 10^{-6}$  Curie, and it was probably of atmospheric origin.

E. H. R.

**The Estimation of Chlorides in Blood.** VICTOR C. MYERS and JAMES J. SHORT (*J. Biol. Chem.*, 1920, **44**, 47—53).—A number of methods for the removal of the proteins of the blood were tried, but none proved as satisfactory as the use of picric acid recommended by Van Slyke and Donleavy (*A.*, 1919, ii, 239). Accordingly, this method is employed, and the estimation is carried out on the same filtrate as is used for the estimation of creatinine and dextrose. The usual Volhard reagents are used in a diluted form and the precipitate of silver chloride is removed by centrifugalisation.

J. C. D.

**The Estimation of Traces of Bromine in Organic Matter.** A. DAMIENS (*Compt. rend.*, 1920, **171**, 799—802).—The organs or organic matter are dried at 100—105°, and the dried material mixed with 5 parts of potassium nitrate and 10 parts of sodium carbonate and heated in a silver crucible to just short of fusion. The mass is extracted with water and the solution filtered. In a portion of the filtrate the iodine, as iodide, may be estimated by Labat's method, or by precipitation as silver iodide, liberation as free iodine by means of chlorine, and colorimetric estimation.

In another portion of the filtrate the whole of the halogens are precipitated as their silver salts, which are afterwards decomposed by zinc and sulphuric acid and the bromine estimated, after filtering off the silver, by the method of Denigès and Chelle (*A.*, 1912, ii, 1208). In the presence of iodide, the iodine is removed from the last filtrate by Labat's method, and then the bromine is estimated as above. Chlorine is estimated by difference from the total halogen content.

W. G.

**Improvement in the Haldane General Air Analysis Apparatus.** ROBERT C. FREDERICK (*Analyst*, 1920, **45**, 409—410).—By making the wide part of the combustion chamber of the apparatus 9 mm. shorter, the stem 25 mm. longer, and placing the mark on the stem 12 mm. from the shoulder, any obscuration resulting from the combustion remains well below the graduation, and frequent cleaning is not required. Owing to the longer stem, the operation of removing globules of mercury from the inlet tap of the apparatus is also facilitated.

W. P. S.

**Simplification of the Kjeldahl Process, particularly for the Estimation of Residual Nitrogen.** ARNOLD HAHN (*Deutsch. med. Woch.*, 1920, **46**, 428—429; from *Chem. Zentr.*, 1920, iv, 399—400).—The serum (1 c.c.) is treated with water (7 c.c.) and phosphotungstic acid (2 c.c.) and centrifuged for several

minutes. Five c.c. of the supernatant liquid are filtered and treated with potassium sulphate, a little copper sulphate, and concentrated sulphuric acid (1 c.c.). The action is complete in about five minutes. (A device for the removal of sulphur trioxide fumes is described and sketched in the original.) The contents of the flask are cooled to about 60° and diluted with water (10 c.c.); after complete cooling, 25 c.c. of alcohol are added. Sodium hydroxide solution (33%, 5 c.c.) is introduced and the ammonia is distilled through an uncooled tube, the end of which is considerably constricted, into sulphuric acid ( $N/100$ , 10 c.c.); excess of the latter is titrated with  $N/100$ -alkali hydroxide solution. Three drops of sodium alizarin-sulphonate solution (1%) and 6 drops of methylene-blue solution (0.05 gram in 100 c.c. of water) are used as indicator; the colour change is from brownish-green to violet. H. W.

**Estimation of Nitrates in Soils.** A. L. WHITING, T. E. RICHMOND, and W. R. SCHOONOVER (*J. Ind. Eng. Chem.*, 1920, **12**, 982—984).—One hundred grams of the soil are shaken for three hours with 300 c.c. of 0.5% hydrochloric acid and allowed to settle for eighteen hours; 200 c.c. of the clear supernatant liquid are then transferred to a flask containing 5 grams of sodium peroxide, and boiled until the volume is reduced to 25 c.c. If urea is present, the evaporation is carried to complete dryness. Two hundred c.c. of water are then added, together with 0.5 gram of Devada's alloy, and the mixture is distilled for forty minutes, the distillate containing the ammonia being collected, as usual, in a definite quantity of standardised acid. W. P. S.

**Detection of Nitrites.** L. THEVENON (*J. Pharm. Chim.*, 1920, [vii], **22**, 336—337).—A red coloration develops at once when a nitrite solution is treated with a few drops of 33% acetic acid and 2 c.c. of 0.5% *p*-aminophenol hydrochloride solution. The reaction, which may be used for the detection of nitrites in drinking water, is not given by nitrates, and the salts occurring in natural waters do not interfere with the test. W. P. S.

**Rapid Colorimetric Methods for the Estimation of Phosphorus in Urine and Blood.** RICHARD D. BELL and EDWARD A. DOISY (*J. Biol. Chem.*, 1920, **44**, 55—67).—The authors take advantage of the fact that certain reducing agents will reduce phosphomolybdic acid in the presence of molybdic acid without affecting the latter. Quinol was selected as the most suitable reducing agent.

If quinol is added to a faintly acid solution of molybdic acid the mixture will be perfectly colourless when treated with a solution of sodium carbonate and sodium sulphite. When phosphates are present, however, a blue colour is produced which can be compared in the usual manner with a standard.

This forms the basis of methods for the estimation of phosphorus and phosphates in urine and blood. It is stated that the results are

not as accurate as those yielded by a suitable gravimetric method, but that the process is a more convenient one for certain purposes.

J. C. D.

**An Extremely Sensitive Colour Test for Phosphates and Arsenates.** G. DENIGES (*Compt. rend.*, 1920, 171, 802—804).—

The reagent used is a mixture of equal volumes of concentrated sulphuric acid and a 10% solution of ammonium molybdate. To 5 c.c. of the liquid containing phosphate or arsenate, 3—10 drops of the reagent, according to the amount of phosphate present, are added. The mixture is shaken, and one or two drops of a freshly prepared solution of stannous chloride are added. A blue colour is obtained in the presence of a phosphate or an arsenate. Fluorides tend to inhibit the reaction, but this can be overcome by the preliminary addition of boric acid if they are present. W. G.

**Estimation of Arsenic and Phosphoric Acids in the Presence of Large Amounts of Salts.** LEON DESBOURDEAUX (*Bull. Sci. Pharmacol.*, 1920, 27, 225—240, 300—313, 363—372).—By the addition of sodium salts to magnesia mixture, magnesium hydroxide is precipitated in amount depending on the quantity of ammonium salt present.

When arsenic is precipitated as magnesium ammonium arsenate, the precipitation is incomplete after thirty-six hours in the presence of ammonium nitrate, ammonium chloride, or ammonium sulphate; in the first two cases complete precipitation is effected in twelve hours by the addition of magnesium nitrate or chloride in amount equivalent to 1/35th of the ammonium nitrate or chloride present. Complete precipitation is inhibited by sodium sulphate, chloride, or nitrate, even in the presence of the corresponding magnesium salt. Precipitation is complete in thirty-six hours in the presence of potassium nitrate, but in the case of potassium chloride magnesium chloride equivalent to 1/35th of the potassium chloride must be added.

Provided an excess of magnesia mixture is used, the precipitation of phosphoric acid as magnesium ammonium phosphate is complete in hot or cold solution in the presence of ammonium nitrate; precipitation is complete in the cold in the presence of ammonium chloride, but not in the hot, whilst in the presence of ammonium sulphate precipitation is incomplete in all cases. Precipitation is incomplete in the presence of sodium nitrate, chloride, or sulphate; with the potassium salts precipitation is satisfactory in warm solutions and is complete in the cold in the cases of the chloride and sulphate.

In estimating phosphoric or arsenic acid as the silver salt in the presence of ammonium, alkali or alkaline earthy nitrate, sulphate, or chloride, the solution is acidified, if necessary, with 5—10 c.c. of concentrated nitric acid, silver nitrate is added in amount corresponding with the chloride and phosphate or arsenate present, and then an excess equivalent to 5% of the ammonium salt or 2% of the

potassium salt present; the mixture is rendered barely perceptibly acid by the addition of ammonia, and after half-an-hour the precipitate is collected, washed with 0.2% silver nitrate, and digested on a boiling water-bath for one hour with 1 vol. of a solution of 40 c.c. of concentrated nitric acid and 4 grams of barium nitrate made up to 1 litre. The solution obtained by filtration is free from chloride and sulphate. The residue in the filter is washed with 2 vols. of a solution of 20 c.c. of concentrated nitric acid, 0.5 gram of barium nitrate, and 4 grams of silver nitrate made up to 1 litre; the combined filtrates are rendered barely acid by ammonia, and the precipitate is collected, washed with 0.2% silver nitrate and with water, dried at 150°, and heated at 400° for two hours before weighing. The method, which is applicable to magnesium ammonium phosphate or arsenate, in general tends to give slightly high results.

CHEMICAL ABSTRACTS.

**Detection of Graphite and its Distinction from Similar Minerals.** O. HACKL (*Verh. geol. Reichsanst. Wien*, 1918, 261—262; from *Chem. Zentr.*, 1920, iv, 399).—Simple methods are indicated for distinguishing between carbonaceous substances and oxides of iron or manganese, metallic manganese, and antimony. The following microchemical method is recommended for the detection of even traces of graphite. The substance is completely freed from carbonates by treatment with boiling dilute hydrochloric acid, after which it is washed and dried. The residue is fused with ten times its weight of potassium nitrate, which converts carbon into carbonates, and the product is extracted with a little water. The presence of carbon is shown by the evolution of carbon dioxide after addition of dilute hydrochloric acid. If only traces of carbon are present, a drop is treated successively with strontium acetate and dilute hydrochloric acid; evolution of gas is then readily observed under the microscope, as is also the eventual re-solution of precipitated strontium carbonate.

H. W.

**Relationship of Hydrogen-ion Concentration of Natural Waters to Carbon Dioxide Content.** R. E. GREENFIELD and G. C. BAKER (*J. Ind. Eng. Chem.*, 1920, 12, 989—991).—The hydrogen-ion concentration of natural waters may be calculated approximately from the simple mass-law equation of the primary ionisation of carbonic acid, namely,  $(H^+)(HCO_3^-)/(H_2CO_3 + CO_2) = 3.0 \times 10^{-7}$  (Landolt and Börnstein), or  $(H^+)(CO_3^{''})/(HCO_3^-) = 6.0 \times 10^{-11}$  (Auerbach and Pick). If hydrogen carbonate and carbon dioxide are expressed in terms of  $CO_2$  per litre,  $(H^+) = 3.5 \times 10^{-7} CO_2 / (HCO_3^-) + 1 \times 10^{-8}$ .

W. P. S.

**Active Carbonic Acid in Drinking Water.** I. M. KOLTHOFF (*Chem. Weekblad*, 1920, 17, 558).—A reply to criticisms, pointing out that the values given by the author (*ibid.*, 390) are not affected by the presence of normal quantities of alkali or magnesium carbonates. [See *J. Soc. Chem. Ind.*, 1920, December.]

S. I. L.

**Estimation of Potassium as Perchlorate. III.** GREGORY P. BAXTER and FRANK E. RUPERT (*J. Amer. Chem. Soc.*, 1920, **42**, 2046—2049. Compare A., 1917, ii, 270; this vol., ii, 388).—The solubility of potassium perchlorate has been determined at 0° and 20° in methyl alcohol, and in ethyl alcohol denaturated with 5% of methyl alcohol, both solvents containing known percentages of perchloric acid. The solubility in methyl alcohol was many times greater than that in the denaturated ethyl alcohol, consequently the former solvent is unsuitable for washing potassium perchlorate in quantitative work. The solubility in the denaturated ethyl alcohol is practically the same as that in pure ethyl alcohol. The procedure previously described for the estimation of potassium (*loc. cit.*) was therefore carried out, using denaturated ethyl alcohol instead of absolute ethyl alcohol. The results show that ethyl alcohol denaturated with 5% of methyl alcohol may safely be substituted for ethyl alcohol in washing potassium perchlorate, and that the temperature at which the washing occurs is unimportant if the washing liquid employed after the initial extraction is previously saturated with potassium perchlorate.  
J. F. S.

**A Microchemical Reaction for Ammonium Salts.** C. VAN ZIJF (*Pharm. Weekblad*, 1920, **57**, 1345—1348).—See this vol., i, 918.

**A New Microchemical "Two-phase Reaction" for Magnesium Ammonium Phosphate.** HERMANN KUNZ-KRAUSE (*Ber.*, 1920, **53**, [B], 1672—1673).—The following reaction, which is best observed microscopically, is specially suited to the detection of magnesium ammonium phosphate in urinary sediments, but may be applied to the detection of phosphates generally. The solution of the sediment in acetic acid is neutralised with ammonia. On addition of a drop of silver nitrate solution, an egg-yellow, cheese-like precipitate of silver phosphate is formed, which disappears on addition of a drop of ammonia. At the same time, the magnesium ammonium phosphate is precipitated as colourless, shining prisms united in the form of rosettes. The reaction may be applied to the detection of phosphates as cellular enclosures in plant tissues.  
E. H. R.

**Microchemical Distinction between Sericite and Talc.** O. HACKL (*Verh. geol. Reichsanst. Wien*, 1918, 241—242; from *Chem. Zentr.*, 1920, iv, 399).—Since sericite (potassium aluminium silicate) frequently contains magnesium and talc (magnesium silicate) often contains aluminium, the qualitative macrochemical tests for aluminium and magnesium give but little information. Complete solution of the mineral is unnecessary for microchemical investigation; it suffices if the finely powdered mineral is extracted with boiling concentrated hydrochloric acid and the solution is evaporated; the residue is dissolved in a little acidified water, and one portion is examined for potassium by means of platinic

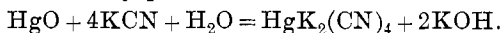


chloride, whilst another part is tested for aluminium with sodium sulphate and caesium chloride. H. W.

**Estimation of Copper (especially in the Analysis of Sugars) by means of Potassium Thiocyanate and Potassium Iodide.** G. BRUHNS (*Zeitsch. anal. Chem.*, 1920, 59, 337—359).—Investigation of the conditions controlling the reaction between cupric salts and a mixture of potassium thiocyanate and potassium iodide showed that the following procedure is trustworthy. Twenty c.c. of Fehling's solution and 20 c.c. of the sugar solution (containing not more than 0.4% of sugar) are mixed, boiled for two minutes, 50 c.c. of cold water are then added, and the whole cooled rapidly. Five c.c. of potassium thiocyanate-iodide solution (potassium thiocyanate, 0.65 gram; potassium iodide, 0.1 gram in 5 c.c. of water) are added, followed by 10 c.c. of 6.5*N*-sulphuric acid, and the liberated iodine is titrated with thiosulphate solution (34.4 grams per litre). A control titration is made at the same time with the same quantities of reagents, but without heating, and the difference between the quantities of thiosulphate solution used for the two titrations is a measure of the reducing sugar present. Tables are given showing the amounts of sugar corresponding with various volumes of thiosulphate solution. W. P. S.

**Colorimetric Analytical Methods. XIII. Estimation of Mercury in Urine.** W. AUTENRIETH and W. MONTIGNY (*Munch. med. Woch.*, 1920, 67, 928—931; from *Chem. Zentr.*, 1920, iv, 426).—A colorimetric method is described for the estimation of mercury in urine as mercuric sulphide with the aid of the Autenrieth-Königsberger colorimeter; other metals precipitable by hydrogen sulphide must not be present. H. W.

**Volumetric Estimation of Mercury, Iron, and Vanadium in the same Solution.** G. HINARD (*Ann. Chim. anal.*, 1920, [ii], 2, 297—299).—To estimate mercury, iron, and vanadium in sulphuric acid solution, an aliquot portion of the latter is treated with hydrogen sulphide, the mercury sulphide separated, oxidised with bromine, the excess of bromine expelled by heating, the solution then rendered alkaline with potassium hydroxide (precipitated mercuric hydroxide does not interfere), a known excess of standardised potassium cyanide solution is added, and the excess then titrated with silver nitrate solution, potassium iodide being added as indicator. The quantity of cyanide used is equivalent to the amount of mercury present:



The filtrate from the mercury sulphide is boiled to expel hydrogen sulphide, oxidised with bromine, and the iron is precipitated as ferric hydroxide by treating the boiling solution with potassium hydroxide; the ferric hydroxide is dissolved in hydrochloric acid, again precipitated as hydroxide (to remove remaining traces of vanadium), then dissolved in sulphuric acid, and estimated iodo-

metrically:  $\text{Fe}_2\text{O}_3 + 2\text{HI} = 2\text{FeO} + \text{H}_2\text{O} + \text{I}_2$ . Iron and vanadium are then determined together iodometrically in a separate portion of the original solution:  $\text{V}_2\text{O}_5 + 2\text{HI} = \text{V}_2\text{O}_4 + \text{H}_2\text{O} + \text{I}_2$ . If the original solution also contains mercurous, ferrous, and vanadyl salts, the first may be separated by treatment with sodium chloride solution, whilst the proportions of ferrous and vanadyl salts may be estimated by iodometric titration before and after oxidation.

W. P. S.

**Rapid Method for the Analysis of Light Aluminium Casting Alloys.** RUSSELL M. BERRY (*J. Ind. Eng. Chem.*, 1920, **12**, 998—1000).—The accuracy of the rapid method described depends on the facts that a larger amount of the alloy can be taken, and that most of the aluminium is removed at the outset from all the other metals, except zinc. The alloy is dissolved in 25% sodium hydroxide solution, and the insoluble residue (tin, copper, lead, iron, nickel, magnesium, part of the manganese, and traces of aluminium) washed with dilute sodium hydroxide solution. The filtrate is acidified with formic acid, the zinc precipitated with hydrogen sulphide, the zinc sulphide digested with hot dilute hydrochloric acid, the liquid filtered, and the filtrate and washings titrated with potassium ferrocyanide solution. Tin is estimated by digesting the alkali-insoluble portion with nitric acid, filtering the solution, washing the residue, and extracting it with ammonium polysulphide and ammonium chloride. The filtrate containing the tin is acidified with acetic acid, and the tin precipitated as sulphide, ignited, and weighed as  $\text{SnO}_2$ . Copper and lead are estimated electrolytically in the first filtrate from the tin, the copper being deposited on the cathode, and the lead on the anode. Iron is precipitated as hydroxide in the electrolyte from the copper and lead estimations, the washed precipitate dissolved in dilute hydrochloric acid, and the iron reduced with stannous chloride and titrated with standard potassium permanganate solution. The filtrate from the iron (and traces of aluminium) is used for the precipitation of the nickel by means of dimethylglyoxime, whilst magnesium is precipitated as phosphate in the filtrate from the nickel. Manganese is estimated by treating the alloy with sodium hydroxide solution, adding nitric acid in excess, and then a few crystals of silver nitrate, oxidising the solution with ammonium persulphate, and titrating it with standard arsenite solution. For the estimation of silicon the alloy is dissolved in a mixture of nitric and sulphuric acids and water, the solution evaporated to dryness, the residue treated with hydrochloric acid and hot water, and the silica ignited, weighed, treated with hydrofluoric acid, and again weighed. [See, further, *J. Soc. Chem. Ind.*, 1920, December.] C. A. M.

**Detection of Manganese in the Presence of Phosphates.** D. H. WESTER (*Ber. Deut. pharm. Ges.*, 1920, **30**, 381—382. Compare this vol., ii, 334, 389).—A further criticism of the method described by Schmidt (*loc. cit.*). W. P. S.

**Detection of Manganese in the Presence of Phosphates.**

ERNST SCHMIDT (*Ber. Deut. Pharm. Ges.*, 1920, **30**, 383).—A reply to Wester (compare preceding abstract). The manganese should be first separated by precipitation as sulphide in order to remove phosphates.

W. P. S.

**Separation of Iron from Aluminium by Precipitation as Prussian Blue.**

HARRISON HALE and G. O. BURR (*J. Amer. Chem. Soc.*, 1920, **42**, 2056—2058).—The quantitative separation of iron from aluminium as Prussian blue cannot be effected, since the aluminium reacts with the excess of potassium ferrocyanide, forming a jelly which cannot be handled. The precipitate of Prussian blue cannot be successfully filtered, even after apparently perfect coagulation.

J. F. S.

**Analysis of Molybdenum, Cobalt, and Chromium Alloys.**

J. R. CAMP and J. W. MARDEN (*J. Ind. Eng. Chem.*, 1920, **12**, 998).—The alloy is dissolved in aqua regia, the excess of which is expelled by heating the solution with 3 c.c. of sulphuric acid. The liquid is cooled, diluted to 100 c.c., saturated with hydrogen sulphide, and heated in a closed bottle for an hour in boiling water. The precipitate of molybdenum sulphide is separated, washed, dissolved, reprecipitated, finally ignited for two hours in a muffle, and the residue weighed as  $\text{MoO}_3$ . The cobalt is precipitated from the boiling filtrate with sodium peroxide, the precipitate washed with dilute hydrogen peroxide, and the black cobaltic hydroxide ignited and weighed at  $\text{Co}_3\text{O}_4$ . In most cases reprecipitation of the cobalt is necessary to ensure complete separation. The filtrate is acidified and the chromates titrated with ferrous ammonium sulphate solution, potassium ferricyanide being used as an external indicator. [See also *J. Soc. Chem. Ind.*, 1920, December.]

C. A. M.

**Identification of Tin in Ores.**

AUGUST ZÖLLER (*Chem. Zeit.*, 1920, **44**, 797—798).—A portion of the mineral or ore is placed on a piece of zinc foil and moistened with a drop of hydrochloric acid; if tin is present a grey film of metallic tin appears on the surface of the mass within a few minutes.

W. P. S.

**Estimation of Gold.**

PAUL DRAWE (*Zeitsch. angew. Chem.*, 1920, **33**, 272).—The following method is recommended for the estimation of gold in alloys also containing silver and copper. From 0.4 to 0.5 gram of the sample is dissolved in aqua regia, the solution evaporated to dryness, and the residue treated with hydrochloric acid and water. After the silver chloride has been separated by filtration, the solution is rendered alkaline with potassium hydroxide, boiled, and the cupric oxide collected on a filter. The filtrate is acidified with hydrochloric acid, then rendered slightly alkaline with potassium hydroxide, hydrogen peroxide is added, the mixture boiled, and the metallic gold collected, ignited, and weighed.

W. P. S.

**Quantitative Organic Microanalysis.** R. CORNUBERT (*Rev. gen. sci.*, 1920, **31**, 442—455).—The paper describes the origin and development of the micro-balance and its manipulation. Detailed descriptions are given for the micro-estimation of carbon, hydrogen, nitrogen, halogens, sulphur, sodium, potassium, calcium, barium, silver, gold, terbium, platinum, chromium, copper, phosphorus, methoxyl, carboxyl, and the :N·OMe group, and for the micro-determination of molecular weights, the methods being essentially those of Pregl and Dubsky.

CHEMICAL ABSTRACTS.

**Use of Reduced Copper in the Elementary Analysis of Organic Compounds.** EMILE CHERBULIEZ (*Helv. Chim. Acta*, 1920, **3**, 652—653).—At a red heat, copper containing small proportions of iron or zinc causes appreciable reduction of carbon dioxide to carbon monoxide, and is, therefore, unsuitable for use in the determination of carbon and hydrogen in nitrogen compounds by combustion or in the estimation of nitrogen (compare Perrot, *Compt. rend.*, 1859, **48**, 53).

T. H. P.

**Absorbent Solution for Heavy Hydrocarbons.** ALEX. PIECHOTA (*Chem. Zeit.*, 1920, **44**, 797).—A saturated solution of potassium dichromate in concentrated sulphuric acid is an efficient absorbent for heavy hydrocarbons in gas analysis.

W. P. S.

**Analysis of Aromatic Nitro-compounds by means of Titanium Chloride.** F. L. ENGLISH (*J. Ind. Eng. Chem.*, 1920, **12**, 994—997).—Mononitro-hydrocarbons are exceedingly resistant to reduction by titanium chloride, but the presence of positive or negative substituents, with the exception of chlorine, in the nucleus facilitates the reduction of the nitro-group. Further, it would appear that the orientation of the substituents with respect to the nitro-group has no appreciable effect; thus, *m*- and *p*-nitroaniline are reduced readily, as are *o*- and *p*-nitrophenols, *o*- and *m*-nitro-*p*-toluidines, and two of the nitrosalicylic acid isomerides. Conversely, *o*- and *p*-chloronitrobenzene are about equally refractory.

W. P. S.

**Detection of Methyl Alcohol as Methyl *p*-Bromobenzoate.** W. AUTENRIETH (*Arch. Pharm.*, 1920, **258**, 1—14).—Methyl alcohol in warm dilute aqueous solution is converted by *p*-bromobenzoyl chloride in presence of 10% sodium hydroxide into the well-characterised and easily crystallisable methyl *p*-bromobenzoate. The test is sufficiently sensitive to detect 0.05 gram of methyl alcohol, even in extreme dilution. The ester is recognisable by its anise-like odour, its m. p., 77—78°, its bromine content by the Carius method, and its conversion by aqueous ammonia into *p*-bromobenzamide, m. p. 188°. The crystalline ester can readily be isolated, even in presence of a large excess of the ethyl ester, which is liquid at temperatures as low as -16°. Thus, from a solution containing 0.2% of methyl and 0.8% of ethyl alcohol,

crystals of the methyl ester were obtained, the method being to extract with ether and crystallise from aqueous alcohol the residue from the ethereal extract. Similarly, 5% of methyl alcohol in a spirit of wine was detected after one fractional distillation. Minute quantities of methyl alcohol in urine can likewise be detected after distilling with phosphoric acid to retain ammonia, and redistilling the distillate with alkali hydroxide to remove phenols. Although the method does not lend itself to an exact estimation of methyl alcohol, yet, when it is a question of the estimation of small quantities in dilute aqueous solution, approximate figures may be obtained, as, according to the results of a series of experiments, fairly constant amounts of 55—65% of the theoretical quantity of methyl *p*-bromobenzoate were isolated. G. F. M.

**Titration with Surface-active Substances as Indicators. IV. The Buffer System in Physiological Solutions (Wort and Beer) as Determined by the Application of Surface-active Substances as Indicators.** WILHELM WINDISCH and WALTHER DIETRICH (*Biochem. Zeitsch.*, 1920, 106, 92—109).—Wort and beer, as well as their ultra-filtrates, show very little capillary activity on addition of *N*/10-sodium hydroxide and *N*/10-hydrochloric acid, which suggests that they contain small quantities of capillary-active fatty acids. Wort and beer are amphoteric, as they manifest a lowering in the surface tension on the addition of sodium undecate (acid indicator) and eucupine dichloride (basic indicator). The titrations indicate the following buffer system in wort: free organic acids—secondary phosphate  $\rightleftharpoons$  primary phosphate—organic salts. On fermenting, the excess of carbon dioxide changes the equilibrium, as follows: free organic acids—bicarbonate  $\rightleftharpoons$  primary phosphate—organic salt (compare this vol., ii, 48, 706, 707). S. S. Z.

**The Colorimetric Estimation of Phenol in Urine.** M. WEISS (*Biochem. Zeitsch.*, 1920, 110, 258—265).—The method described by the author for the estimation of tyrosine with Millon's reagent (this vol., ii, 135) can also be employed for the estimation of hydroxyphenyl derivatives in urine. The latter have, however, to be previously liberated from the acids with which they are combined by means of hydrolysis. In disease, there is an increase in the excretion of phenol. S. S. Z.

**Estimation of Very Small Quantities of Dextrose.** PERRIER (*J. Pharm. Chim.*, 1920, [vii], 22, 337—344).—A method, proposed originally by Bougault (*A.*, 1917, ii, 395), and depending on the oxidation of aldoses by iodine in alkaline solution, is applicable to the estimation of very small quantities of dextrose. Two hundred c.c. of the sugar solution (containing about 0.17 gram per litre) are mixed with 200 c.c. of *N*/200-iodine solution and about 7 c.c. of 1.5% sodium carbonate solution, and the mixture is diluted to 1000 c.c.; after two hours, the mixture is acidified with hydrochloric acid and titrated with *N*/100-thiosulphate solution.

0.2 C.c. is deducted from the volume of iodine solution required to oxidise the sugar. The method may be used for the estimation of dextrose in body fluids.

W. P. S.

**Preservation of Specimens of Blood intended for Blood-sugar Estimations.** W. DENIS and MARTHA ALDRICH (*J. Biol. Chem.*, 1920, **44**, 203—206).—One drop of commercial formaldehyde to 5 c.c. of oxalated blood appears to be a satisfactory preservative. It does not interfere with the subsequent estimation.

J. C. D.

**Folin and Wu's Methods for the Estimation of the Sugar and the Nitrogenous Constituents of the Blood.** R. DELABY (*Bull. sci. pharmacol.*, 1920, **27**, 372—374).—A review of the latest method of Folin and Wu for the estimation of sugar in the blood, and the statement that these authors advocate in correspondence the use of a urease paper for the estimation of urea. This paper is made by dipping filter paper into the filtrate from a mixture of 30 grams of jack-bean powder, 15 grams of permute, and 200 c.c. of 16% ethyl alcohol. Two to three sq. cm. of the paper are used for each estimation.

CHEMICAL ABSTRACTS.

**Estimation of Small Amounts of Reducing Sugar in the Body Fluids.** L. DE SAINT-RAT and J. RONFAUT (*Bull. sci. pharmacol.*, 1920, **27**, 289—293).—To 5 c.c. of solution containing from 0 to 8 mg. of reducing sugar are added 5 c.c. each of Bertrand's copper and alkali solutions, and the mixture is placed in a boiling-water bath for twenty minutes. To prevent evaporation, a glass bulb is placed in the mouth of the tube. Identical conditions of dilution must be scrupulously observed. The blank obtained with water and the 10 c.c. of alkaline copper solution under these conditions is equivalent to 0.78 mg. of copper. The copper oxide formed is filtered on asbestos by gentle suction in such a way as to prevent undue contact with air. This is accomplished by closing the filtering tube with a perforated stopper, through which passes a glass tube to the reaction test-tube, the contents of which are slowly aspirated over into the filtration tube by the same suction stream that brings about filtration. The precipitate is dissolved by intermittently aspirating two 5 c.c. lots of ferric solution (which has been proved to have no reducing action on permanganate solution) through the tube. The reaction test-tube is washed twice with 5 c.c. of the ferric solution, and the tube and filter are washed with water. The filtrate is titrated with 0.2N-permanganate prepared according to Halversen and Bergheim's method. A table and chart are given of the mg. of dextrose per mg. of copper obtained. Body fluids, such as cerebrospinal fluids, are deproteinised by first heating the solution on the water-bath with equal amounts of zinc and lead acetates, as measured on the tip of a knife blade, and filtering.

CHEMICAL ABSTRACTS.

**Identification of Acids by Phenacyl Bromide.** H. E. Cox (*Analyst*, 1920, **45**, 412).—When using phenacyl bromide (*o*-bromoacetophenone) for the esterification and identification of acids (compare Rather and Reid, A., 1919; i, 157), care should be taken that the substance does not come into contact with the skin, since even small quantities produce very painful blisters.

W. P. S.

**Comparison of Methods for Estimating the Iodine Number of Fats.** W. DEVRIENT (*Ber. Deut. pharm. Ges.*, 1920, **30**, 361—366).—Estimations of the iodine number of elaidic acid by different methods yielded the following results: Hübl method, 80·3; Waller method, 80·0; Winkler method, 80·8; Wijs method, 80·8; Hanuš method, 82·5. The author prefers the last method, as being the most simple and rapid, and because the result obtained is nearer the theoretical value, 90, than are those given by the other methods.

W. P. S.

**Microchemical Detection of Cyanic Acid.** R. FOSSE (*Compt. rend.*, 1920, **171**, 722—723).—Silver cyanate crystallises from hot aqueous solution in a definite microcrystalline form, by means of which it can be identified. When silver cyanate, potassium chloride, and cobalt acetate are ground together in the solid state, a deep blue colour is obtained, which disappears on the addition of water and reappears on the addition of alcohol. The blue colour is due to the formation of potassium cobalticyanate, which may be distinguished from the cobaltithiocyanate in that only the latter gives a colour with amyl alcohol. Dilute acids do not destroy or decolorise the cobalticyanate. Ferric chloride gives a red colour with the cobaltithiocyanates, but not with the cobaltcyanates. Finally, if silver cyanate is ground with hydroxylamine hydrochloride, and a drop of ferric chloride solution added to the product, a violet-blue coloration is produced.

W. G.

**Estimation of Urea in Blood by Xanthhydrol.** W. MESTREZAT and (MLLE) MARTHE PAUL JANET (*J. Pharm. Chim.*, 1920, [vii], **22**, 369—377).—See this vol., ii, 645.

**Identification of Sulphonal and Trional.** WALTHER ZIMMERMANN (*Apoth. Zeit.*, 1920, **35**, 27).—Sulphonal has m. p. 125—126°, and trional has m. p. 76°. When 0·1 gram of sulphonal or trional is heated in a test-tube with 0·1 gram of sodium salicylate, an odour of mercaptan is observed; if the mixture is treated with five drops of alcohol and five drops of concentrated sulphuric acid, and, after five minutes, heated with the addition of a further five drops of sulphuric acid, a turbid, red solution is obtained, which has an odour of methyl salicylate. A violet-coloured residue is obtained when a mixture of 0·2 gram of sulphonal or trional and 0·02 gram of sodium salicylate is ignited in a porcelain basin; this residue gives a violet solution

when treated with a drop of water. The addition of a drop of dilute hydrochloric acid changes the colour to yellow, a brown, flocculent precipitate separates, and sulphur dioxide is evolved. Acetanilide, antipyrin, and phenacetin yield black residues when heated with sodium salicylate, veronal a green residue, and santonin a red residue.

W. P. S.

**Behaviour of Silico- and Phospho-tungstic Acids towards Alkaloids.** A. HEIDUSCHKA and L. WOLFF (*Schweiz. Apoth. Zeit.*, 1920, **58**, 213—218, 229—233).—For gravimetric estimations with silicotungstic acid, a 0.01*N*-solution of the acid (of pre-determined water content) is prepared and standardised by means of a 0.01*N*-solution of a quinine salt in the presence of 1% hydrochloric acid; the precipitate is collected and incinerated, and the factor is calculated from the weight of the residual  $\text{SiO}_2, 12\text{WO}_3$ .

The compounds were examined as follows. A 0.01*N*-solution of the alkaloid is prepared equivalent to 4 mols.:1 mol. of silicotungstic acid. Corresponding volumes of the alkaloid and silicotungstic acid solutions are mixed, 1% hydrochloric acid is added, and the precipitate is collected after one hour. With quinine, cinchonine, papaverine, and narcotine, precipitation occurs readily; coniine in small quantities is not precipitated. Quinine, cinchonine, sparteine, and nicotine form compounds of the type  $\text{SiO}_2, 12\text{WO}_3, 2\text{H}_2\text{O}, 2\text{B}, x\text{H}_2\text{O}$  (or  $\text{Si}:\text{B}=1:2$ ). Caffeine with 1% hydrochloric acid is barely precipitated, but with 3% hydrochloric acid a 1:3-compound is obtained. Morphine, codeine, thebaine, atropine, and cocaine yield 1:4-compounds. Morphine in the presence of 1—3% sodium chloride yields a 1:2-compound; with strychnine, brucine, narcotine, papaverine, colchicine, aconitine, and veratrine, more silicotungstic acid is contained in the precipitate with greater concentrations of the electrolyte, but at lower concentrations the equilibrium is displaced towards the ratio 1:4. When precipitated from dilute alcoholic solution (in the absence of hydrochloric acid), strychnine, brucine, veratrine, and aconitine yield exactly 1:4-compounds.

In volumetric analysis, a moderate excess of the silicotungstic acid solution is added, then 1% sodium chloride, and, after filtering, the solution is titrated with sodium hydroxide with methyl-red as indicator; the method is inapplicable in the presence of albumin.

For the gravimetric estimation of alkaloids with phosphotungstic acid, the latter is used in 0.01*N*-solution, the factor being determined as above from the weight of  $\text{HPO}_3, 12\text{WO}_3$  obtained after incineration. With quinine, cinchonine, sparteine, and nicotine, the ratio  $\text{P}:\text{alkaloid}=2:3$ , the formula of the compound being  $2[\text{P}(\text{W}_2\text{O}_7)_6]\text{H}_7, 3\text{B}$ ; this composition is constant when the precipitation is effected in the presence of less than 1% of hydrochloric acid. With all other alkaloids, the ratio is 1:3 at low concentrations of hydrochloric acid. This method is preferable to the silicotungstic acid method for aconitine and nicotine.



Small amounts of alkaloids can be estimated by means of the opalescence produced with silico- or phospho-tungstic acid.

CHEMICAL ABSTRACTS.

**The Conductometric Titration of Alkaloids and their Salts.** I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, **112**, 196—208).—Alkaloids or their salts can be titrated with satisfactory accuracy by the conductometric method in very dilute solutions. The alkaloids themselves are titrated with acid; the conductivity rises steadily from the commencement of the titration, and at the point where salt formation is complete, the rate of increase of conductivity suddenly augments. The alkaloid salts are titrated with alkali, and in these cases, also, the conductivity curve rises throughout the titration, with a sharp break at the neutral point. In the case of a basic salt, such as quinine hydrochloride, in which the second dissociation constant is not too small, the acid content can be determined by titration with alkali and the alkaloid by means of acid. Titrations of alkaloids or their salts with indicators, such as phenol- or thymol-phthalein for alkali and methyl-red or dimethyl-yellow for acid titration, generally give uncertain results, because a solvent, such as alcohol or chloroform, has to be used. For the conductometric titration of the alkaloid salts, no solvent need be used, but for the titration of the free alkaloids they are generally dissolved in 55% alcohol. The alkaloid salts examined included quinine hydrochloride, strychnine nitrate, cocaine and tropacocaine hydrochlorides, novocaine, atropine sulphate and morphine and ethylmorphine hydrochlorides. In the case of morphine hydrochloride, it was found best to titrate in 50% alcohol; no distinct break was found in the conductivity curve at the neutral point, but, on continuing the titration with alkali, morphinate formation was indicated by a very sharp break in the curve. The alkaloid bases examined included quinine, hydrastine, codeine, morphine, nicotine, theobromine, and caffeine. The last is a very weak acid with a dissociation constant less than  $10^{-14}$ , whilst that of theobromine is about  $10^{-10}$ . Accordingly, it was found that theobromine could be exactly estimated in a mixture with caffeine by dissolving in alkali and titrating back with acid. The break in the conductivity curve was quite distinct.

E. H. R.

**Estimation of Cystine.** Y. OKUDA (*J. Coll. Agr. Imp. Univ. Tokyo*, 1919, **7**, 69—76).—The cystine should be present in a solution with a volume of 10 c.c. and containing from 5 to 10% of hydrochloric or sulphuric acid. To this solution are added 10 c.c. of 20% sodium bromide solution. The cystine is now titrated with 0.05*N*-sodium bromate, taking as the end-point a faint yellow colour, which remains for one minute; 1 c.c. of the bromate solution equals 0.00721 gram of cystine. The cystine is oxidised to cysteic acid by bromine, which is formed by the reaction between

the bromide and bromate in the acid solution; 1 mol. of cystine requires 10 atoms of bromine in this oxidation. Of the amino-acids, other than cystine, which are precipitated by phosphotungstic acid, only histidine absorbs bromine; however, the velocity of the reaction between cystine and bromine is so much greater than that of the reaction between histidine and bromine that the presence of histidine does not influence the titration of cystine, provided the titration be stopped when the solution becomes faintly yellow, and the colour remains constant for one minute. Even as small an amount of cystine as a few mg. may be accurately estimated by this method; the result is not influenced by the concentration of either the cystine or the acid. If a solution contains both cystine and tyrosine, the latter will react with 2 atoms of bromine. The titration is made as usual; the cystine is oxidised and estimated as barium sulphate, and the tyrosine is calculated, or the tyrosine is estimated colorimetrically, and the cystine is calculated. This procedure may be applied in analysis of the cleavage products of proteins.

CHEMICAL ABSTRACTS.

**Estimation of Morphine in Opium.** AXEL JERMSTAD (*Ber. Deut. pharm. Ges.*, 1920, **30**, 398—402).—The following modification of the Helfenberger method is recommended: 6 grams of the powdered opium are ground with 6 grams of water, the mixture is rinsed into a flask, and water is added to make the total weight 54 grams. After thirty minutes, the mixture is filtered, 40 grams of the filtrate are treated with 2 grams of ammonia solution (17 grams of ammonia and 83 grams of water), filtered, and 36 grams of this filtrate are shaken for ten minutes in a flask with 7 grams of ether and 4 grams of ammonia; 10 c.c. of ether are then added, and, after thirty minutes, the ethereal solution is poured through a small filter. The crystals in the flask are washed with 10 c.c. of ether, then with three successive quantities of 5 c.c. of water saturated with ether, and dried at 100°. The crystals are then dissolved in 25 c.c. of *N*/10-hydrochloric acid, 75 c.c. of water are added, and the excess of acid is titrated with *N*/10-sodium hydroxide solution, using methyl-red as indicator. One c.c. of *N*/10-acid is equivalent to 0.0285 gram of anhydrous morphine.

W. P. S.

**New Method for the Estimation of the Total Minor Alkaloids, of Narcotine, and of Papaverine in Opium Preparations of the Type of Pantopon.** E. ANNELEER (*Arch. Pharm.*, 1920, **258**, 130—137. Compare A., 1912, ii, 818).—The following process for the estimation of the total minor alkaloids (with the exception of narceine) is recommended. The mixture of hydrochlorides (1.5 grams) is dissolved by warming in water (8 c.c.), and pure benzene (90 grams) is added. Powdered sodium carbonate (0.5 gram) is gradually added with shaking, and the mixture is allowed to remain for half an hour, with frequent

vigorous agitation. Water is absorbed by the addition of anhydrous sodium sulphate (5 grams), followed by agitation during five minutes, and further addition of tragacanth powder (0.5 gram). After thirty minutes, the benzene solution is rapidly filtered, and 80 grams of it (or other aliquot portion) are evaporated to dryness in a tared flask on the steam-bath. The residue is dissolved in a few c.c. of warm alcohol, the solvent is removed, and the residue weighed after being dried for half an hour in the steam-oven. The results agree with those obtained by the method of Mannich and Schwede, to which the empirical correction of 1.5% has been made.

Narcotine and papaverine are estimated in the minor alkaloids in the following manner. The minor alkaloids (obtained in the process outlined above) are dissolved in benzene (6 c.c.), the solution is treated with 1 c.c. of alcoholic potassium hydroxide solution (1 c.c. = 0.14—0.16 gram KOH), and the mixture is allowed to remain at the ordinary temperature, with frequent shaking, during half an hour. It is then poured into a separating funnel (100 c.c.), the flask is rinsed with three portions of benzene (each 10 c.c.), and subsequently three times with aqueous sodium hydroxide solution (2%; 7 c.c. each time), and the solution is well shaken in the separator. The aqueous solution is run into a second separating funnel, and the benzene solution is twice washed with sodium hydroxide solution (10 c.c. each time). The combined aqueous extracts are shaken with three portions of chloroform (5 c.c.) and run into a beaker, where, after being neutralised with hydrochloric acid, they are diluted to 100 c.c. Concentrated hydrochloric acid (36%; 3 c.c.) is added, and the solution is heated for twenty minutes at 80—90°, immediately cooled, and poured into a separating funnel; after addition of an excess of sodium carbonate solution, the narcotine is extracted with benzene (20+10+10+5 c.c.) or chloroform. The extract is dried with a little tragacanth powder and filtered into a weighed flask, and evaporated to dryness on the water-bath; the residue is again dissolved in a little warm alcohol, the solvent is removed, and the residue dried and weighed.

The benzene solution remaining in the separating funnel (see above) is filtered into a flask and evaporated to dryness, the chloroform extract being similarly treated in the same flask. The residue is dissolved in a mixture of water (10 c.c.) and hydrochloric acid (10%; 1 c.c.), the solution is filtered into a small beaker, and the filter paper thrice washed with water (5 c.c.). Ammonia solution (2%) is cautiously added until a faint, permanent turbidity results, followed by solid sodium acetate (2 grams). The mixture is allowed to remain for twenty-four hours, with frequent stirring and rubbing of the walls of the beaker, whereby the papaverine is precipitated as a glassy or powdery mass. The mother liquor is passed through a small filter, which is subsequently washed three times with water (5 c.c.). The paper is returned to the beaker,

and, after both have been dried, the papaverine is dissolved in warm alcohol. The solution is filtered into a weighed flask, the solvent is removed, and the residue is weighed after being dried during an hour at 98°.

The method is applied to opium powder in the following manner. The powder (6.66 grams) is frequently shaken in a corked flask during three hours with a mixture of water (115 c.c.) and hydrochloric acid (10%; 5 c.c.), and the paste is then filtered by means of a suction pump. 102 C.c. of the filtrate (=5.55 grams of opium powder) are rendered alkaline by the addition of sodium carbonate solution (10%; 23 c.c.), and extracted with chloroform (20 + 10 + 10 + 10 c.c.). The extract is dried with a little tragacanth powder, filtered, and evaporated to dryness after addition of alcohol (5 c.c.). The residue is dissolved in hydrochloric acid (1%; 8–10 c.c.), the solution is agitated with benzene (100 c.c.) and sodium carbonate (1 gram) during fifteen minutes, and the estimation is completed as with pantopon.

H. W.

### **Proteinogenous Amines. VII. Colorimetric Estimation of Histidine in Protein and Protein-containing Matter.**

MILTON T. HANKE and KARL K. KOESSLER (*J. Biol. Chem.*, 1920, **43**, 527–542).—The method is stated to be simple, rapid, and direct, but may be no more accurate than those described by Kossel and Kutscher and by Van Slyke.

The material is hydrolysed by boiling with hydrochloric acid, and the acid and any volatile phenols removed by vacuum distillation. Ammonia and humin are removed by treatment with lime, and the solution divided into two fractions by means of phosphotungstic acid. The phosphotungstate precipitate is treated with water and sufficient 3*N*-sodium hydroxide to give a clear solution, which is then used for the colorimetric determination by the method previously described (Koessler and Hanke, this vol., ii, 67). The method cannot be used for estimations on protein material that has undergone putrefactive changes, since histamine and tyramine are precipitated by the phosphotungstic acid and give the colour reaction.

J. C. D.

**The Separation of Histidine from Arginine.** H. KOSSSEL and S. EDLBACHER (*Zeitsch. Biol. Chem.*, 1920, **110**, 241–245. Compare A., 1907, i, 107).—The presence of arginine is not necessary in order to effect the precipitation of histidine.

S. S. Z.

### **Proteinogenous Amines. VIII. Colorimetric Estimation of Histamine in Protein and Protein-containing Matter.**

MILTON T. HANKE and KARL K. KOESSLER (*J. Biol. Chem.*, 1920, **43**, 543–556).—A dry solid is hydrolysed directly with 20% hydrochloric acid for thirty hours. When the material contains

water, it must first be treated with alcohol until the concentration of this solvent is 75%. The mixture is then made faintly acid with acetic acid, and the proteins are coagulated by heating on the water-bath for one or two hours. The mixture is cooled and filtered, and the alcohol removed from each fraction by evaporation. The dry material is employed for hydrolysis. After the hydrolysis is completed, the hydrochloric acid is removed by vacuum evaporation at 60°, and the residue is dried at 80° for one hour.

Ammonia is removed by another vacuum distillation after an excess of lime and dilute alcohol have been added, and by filtration of the fluid after the ammonia has been removed, the humin matter is also separated.

The alkaline filtrate is acidified with hydrochloric acid, and basic substances precipitated with phosphotungstic acid. This precipitate, which contains the proteinogenous amines as well as the dibasic amino-acids, is well washed and decomposed with hot saturated solution of barium hydroxide. After removal of the excess of barium from the filtrate by sulphuric acid, the liquid is evaporated to dryness and dissolved in a very small quantity of water, and made up to known volume. The histamine is extracted from an aliquot portion of this liquid by making strongly alkaline with solid sodium hydroxide and extracting with amyl alcohol several times. The combined amyl alcohol extracts are washed several times with normal sulphuric acid, and the acid fractions neutralised with barium hydroxide while warm. The filtrate from the barium sulphate contains all the histamine, but may also contain traces of histidine. A re-extraction with amyl alcohol after making alkaline with sodium hydroxide is necessary to separate these two substances entirely. From the histamine fraction the histamine is precipitated by silver nitrate and baryta, and the resulting silver compound decomposed by means of hydrochloric acid. The final histamine fraction is then estimated colorimetrically, as described in a previous paper (this vol., ii, 67). Quantities as small as 0.1 mg. of histamine can be accurately determined by this method, even in the presence of protein substances. No evidence of the presence of histamine in caseinogen could be detected by this method, but this protein may contain a substance which possesses a similar depressor action when tested by physiological methods.

Histamine was not found present in 75 c.c. of human blood serum.

J. C. D.

**Use of Ethyl Acetate as a Precipitating Reagent for Proteins.** A. MARIE (*Bull. Sci. Pharmacol.*, 1920, 27, 135—136; from *Chem. Zentr.*, 1920, iv, 315. Compare this vol., ii, 398).—The detection of protein by the turbidity which results when its aqueous solution is covered with a layer of ethyl acetate is more readily effected in this manner than with any other organic solvent which is soluble in water.

H. W.

**The Influence of Tyrosine and Tryptophan on the Coloration of the Two Phases of the Xanthoproteic Reaction.** CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1919, 107, 203—210).—The intensity of the coloration produced by tyrosine and tryptophan in the acid phase (phase *a*) and in the alkaline phase (phase *b*) in the xanthoproteic reaction was estimated quantitatively against standard solutions of normal potassium chromate and dichromate and a mixture of dichromate and permanganate. The results showed that, in phase *a*, tryptophan reacted three times as intensely as tyrosine; in phase *b*, on the other hand, tyrosine yielded a coloration five times as intense as that caused by tryptophan; in other words, tryptophan acts three times as intensely in phase *b* as in phase *a*, whilst the coloration yielded by tyrosine in phase *b* is forty-five times as strong as that yielded by it in phase *a*.  
S. S. Z.

**Some Biochemical Colour Tests. II. The Adamkiewicz Protein Reaction. The Mechanism of the Hopkins-Cole Test for Tryptophan. A New Colour Test for Glyoxylic Acid.** WILLIAM ROBERT FEARON (*Biochem. J.*, 1920, 14, 548—563. Compare A., 1918, ii, 462).—On warming with 1% pyrogallol in sulphuric acid, glyoxylic acid gives a deep blue colour, changing to carmine when the liquid is diluted with water; it is restored when an excess of sulphuric acid is again added. The blue colour is not given by oxalic acid or by any of its simple derivatives, which do not give rise to glyoxylic acid under the conditions of the test. With the aliphatic aldehydes, a red colour is given. An intermediate shade of purple is given by formaldehyde in the presence of glyoxylic acid, and the test is of value in the detection of aldehydes in ether. Syrupy phosphoric acid may also be used in place of sulphuric. The chemistry of the test has not been completely investigated. The coloured condensation products are probably hydroxy-derivatives of xanthen. On applying this reagent to solutions of formaldehyde in sulphuric acid in the presence of oxidising agents, under conditions of the Rosenheim test (A., 1906, ii, 508), no evidence of the formation of glyoxylic acid was obtained. This supports the view expressed by Rosenheim that the test depends on formaldehyde. It appears probable, however, that both formaldehyde and glyoxylic acid form coloured derivatives with tryptophan.

Sulphuric acid is not a good condensing agent for these tests. and use was made of glacial acetic acid saturated with hydrogen chloride or phosphoric acid. For production of a coloured condensation product, however, an oxidising agent, such as hydrogen peroxide, is necessary. The separation of the condensation products was found to be difficult, but was attained by fractional precipitation with pure ether.

A number of condensation products have been prepared. The leuco-compounds are somewhat unstable, readily being oxidised to the coloured complexes.

As precipitated, the pigments are all hydrochlorides of nearly colourless bases. The free pigments are amorphous, deeply coloured powders showing melting points in the region of  $300^{\circ}$ .

The following compounds are described: *scatole-formaldehyde-red*,  $C_{19}H_{16}N_2X$ ; *scatole-glyoxylic-red*,  $C_{20}H_{16}N_2X$ ; *scatole-benzaldehyde-purple*,  $C_{25}H_{20}N_2X$ . Similar condensation products of tryptophan with formaldehyde, glyoxylic acid, and benzaldehyde are described. Brief reference is made to condensation products of carbazole and aldehydes. The formation of these pigments constitutes a good test for carbazole. Salicylaldehyde is recommended as a useful qualitative reagent for indole derivatives.

J. C. D.

**Detection of Albumin in Urine.** WILHELM RADO (*Gyógysz. 6*, 66—67; from *Chem. Zentr.*, 1920, iv, 400).—The test is applied by the addition of sulphuric acid (5%; about 1 c.c.) and sodium nitroprusside solution (eight to ten drops) to the filtered urine (5—10 c.c.); in sensitiveness and clinical applicability, the test is equal to Boedeker's method with potassium ferrocyanide and acetic acid.

H. W.

**Estimation of Albumin in Urine by means of Aufrecht's and Esbach's Albuminimeters.** BRUNO WIENSS (*Pharm. Zentr.-h.*, 1920, 61, 535—537).—Comparative estimations showed that the results obtained by the Aufrecht apparatus agreed closely with those found by the gravimetric method, whilst in every case the Esbach results were too high.

W. P. S.

**Gravimetric Estimation of Albumin in Urine.** G. PÉGURIER (*Ann. Chim. anal.*, 1920, [ii], 2, 332—335).—The estimation of albumin in urine may be accelerated by combining the method of heating with Méhu's method of precipitation with phenol. For this purpose, a modified reagent, consisting of 10 grams of colourless, crystallised phenol, 10 grams of powdered citric acid, and 20 grams of 95% alcohol, is used. The urine is rendered distinctly acid to turmeric by means of acetic acid, and filtered, and 50 c.c. of the filtrate heated to incipient boiling, left for a few minutes, and then treated with 5 c.c. of the reagent and the flask shaken with a rotatory movement. As soon as the precipitate is coagulated, the liquid is filtered through counterpoised filter papers, and the precipitate washed first with boiling water and finally with a mixture of alcohol and ether, and dried at  $100^{\circ}$  until constant in weight.

C. A. M.

**Action of Hydrogen Peroxide on Flours.** MARION (*Compt. rend.*, 1920, 171, 804—806).—The amount of catalase differs from one sample of flour to another. It is most prevalent in milling offals and least in high-grade flour. Measurement of the amount of decomposition of a definite volume of hydrogen peroxide by a given weight of flour in a given time gives a means of determining the percentage of extraction of the flour.

W. G.

**The Indices of Enzymes of the Blood. Estimation of the Catalase, Peroxydase and, Esterase in a Drop of Blood.** A. BACH and (MME) SOPHIE ZOUBKOFF (*Compt. rend.*, 1920, **171**, 967—969).—For the test, 0.02 c.c. of the blood is diluted with 20 c.c. of water, and 1 c.c. of this solution is used for each test. The catalase activity is measured by the amount of hydrogen peroxide decomposed under given conditions and the peroxydase activity by the amount of guaiacol oxidised in the presence of hydrogen peroxide as compared with the effect from 1 c.c. of the diluted blood, previously boiled. This estimation is colorimetric. For the measurement of the esterase activity, advantage is taken of the fact that phenolic esters are not oxidised by the system peroxydase-hydrogen peroxide, whereas free phenols are readily oxidised.

W. G.

**Biological Methods for the Estimation of Substances which Injure the Cell and its Reproducing Capacity.**

**1. Optochin.** ALFRED SCHNABEL (*Biochem. Zeitsch.*, 1920, **108**, 258—279).—Dilutions of optochin of one in several millions can be estimated by utilising its action on the reduction of methylene-blue by *Pneumococci*. The greatest dilutions can be estimated at the ordinary temperature, but more exact results are obtained at a temperature of 37°. The concentrations of optochin solutions which can be estimated are also influenced by the number of bacteria and the duration of action.

S. S. Z.

**Measurement of the Lachrymatory Power of Irritant Substances by the "Sill" Method.** CHARLES DUFRAISSE and JACQUES CH. BONGRAND (*Compt. rend.*, 1920, **171**, 817—819).—The method consists in determining the concentration of the substance required in an atmosphere just to produce the first irritant sensation on the eyes at the end of thirty seconds' exposure. Benzyl bromide was taken as the standard. By this method, the lachrymatory power was independent of the observer, although the actual concentration for the gases might vary in the same proportion from one observer to another.

W. G.

**The Properties of Lachrymatory Substances and the Measure of their Activity.** GABRIEL BERTRAND (*Compt. rend.*, 1920, **171**, 965—967).—It is shown that the minimum concentration of a lachrymatory substance which is perceptible depends, not only on the observer, but on the duration of the exposure. With some substances the effect is immediate, and increases but little in intensity with time, whilst with others there is marked increase in intensity with the time. In consequence, the method of Dufraisse and Bongrand (preceding abstract) does not give a correct comparison between different lachrymatory substances.

W. G.



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# ERRATA.

## VOL. CXII (ABSTR., 1917).

- | Page   | Line |   |
|--------|------|---|
| i. 277 | 4    | for "3:6-dimethyl-1:4-benzopyrone" read "3:6-dimethyl-2:3-dihydro-1:4-benzopyrone." |
| ,,     | 13   | for "3:6-dimethyl-1:4-benzopyrone" read "3:6-dimethyl-2:3-dihydro-1:4-benzopyrone." |

## VOL. CXIV (ABSTR., 1918).

- |         |    |                                       |
|---------|----|---------------------------------------|
| ii. 366 | 20 | for "tetradimite" read "tetradymite." |
| ,,      | ,, | for "grunlingite" read "grünlingite." |

## VOL. CXVI (ABSTR., 1919).

- |         |     |  |
|---------|-----|--|
| ii. 337 | 14* | for "Aktiebolag" read "Aktiebolag."  |
| ii. 563 | 28* | col. ii. insert "Jackson, Leonard C., mathematical investigation of the stability of A. W. Stewart's atom, ii, 405." |

## VOL. CXVIII (ABSTR., 1920).

- | Page    | Line |   |
|---------|------|---|
| i. 75   | 13   | } for "Chelidoneum" read "Chelidonium."   |
|         | 14   |   |
| i. 131  | 18*  | } "Heterotropic" read "Heterotrophic."  |
|         | 5*   |   |
| i. 131  | 24*  | "L. E. SANDO" read "C. E. SANDO."   |
| i. 159  | 17*  | "EISNER" read "ELSNER."   |
| i. 207  | 1    | "Potassium" read "Calcium."   |
| ,,      | 3    | "Potassium" read "Calcium."   |
| i. 389  | 5*   | "ZEILER" read "ZELLER."   |
| i. 391  | 8    | "CASTALDI" read "GASTALDI."   |
| i. 438  | 5    | "3-p-hydroxy-m-methoxymeconine" read "3-p-hydroxy-m-methoxy-phenylmeconine."  |
| i. 561  | 7    | "5:7-dimethoxyacetyl-3-methoxycoumarin" read "5:7-dimethoxy-acetoxy-3-methoxycoumarin."   |
| i. 659  | 11*  | "CAPELLI" read "CAPPELLI."  |
| i. 726  | 5    | "OMe. C <sub>6</sub> H <sub>4</sub> . CH. CH <sub>2</sub> . OMe" read "OMe. C <sub>6</sub> H <sub>4</sub> . CH <sub>2</sub> . CH <sub>2</sub> . OMe."   |
| ii. 199 | 3*   | "HELDT" read "HILDT."   |
| ii. 237 | 15   | "26" read "12."   |
| ii. 298 | 10   | "Busting" read "Roasting."  |
| ii. 308 | 5*   | "3H <sub>2</sub> PO <sub>4</sub> " read "3H <sub>3</sub> PO <sub>4</sub> ."   |
| ii. 441 | 23   | "Ütö" read "Utö."   |
| ,,      | ,,   | "Foren." read "Fören."  |
| ,,      | 25   | "p > v" read "ρ > v."   |
| ,,      | 27   | "33·54" read "33·64."   |
| ,,      | ,,   | "104·27" read "104·37."   |
| ii. 503 | 11*  | "Contact with hydrogen, owing to surface combustion, raises the temperature of one helix," read "Contact with hydrogen, owing to the change in thermal conductivity of the gas, lowers the temperature of one helix." |
| ii. 729 | 23*  | "REICHENSTEIN" read "REICHINSTEIN."   |
| ii. 753 | 20   | "GARNER, and DOROTHY WEBSTER" read "GARNER, FREDERICK CHALLENGER, and DOROTHY WEBSTER."   |

\* From bottom.